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A STUDY OF THE PLATE FACTORS IN THE FRACTIONAL DISTILLATION OF THE ETHYL ALCOHOL–WATER SYSTEM

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A STUDY OF THE PLATE FACTORS IN THE FRACTIONAL DISTILLATION OF THE ETHYL ALCOHOL–WATER SYSTEM

I. Introduction

1. *Objects of Investigation.*—The importance of fractional distillation as a unit operation of chemical engineering is well known. It is also common knowledge that, at the present time, a fractionating column cannot be satisfactorily designed because individual plate efficiencies cannot be determined until the column is actually built and operated. This investigation was undertaken essentially in order to add to the knowledge of the effect of certain factors on plate efficiencies with particular reference to the ethyl alcohol–water system and to the bubble-cap plate.

The binary system, ethyl alcohol–water, was chosen for the investigation because of its commercial importance and because its physical properties are well known.

The primary aims of this investigation comprised, first, the development of an experimental procedure by which plate efficiencies might be determined directly from samples of both vapor and liquid streams; second, the determination of the effect on plate efficiencies of variations in liquid composition, particularly at very low and at high compositions, in vapor velocities below the point of entrainment, and in reflux ratio; and third, an evaluation of these influences in terms of the physical properties involved.

2. *Work of Previous Investigators.*—As Underwood[16*] has mentioned in his survey of the field, fractional distillation has been quantitatively investigated by many contributors to the literature. The simplest example of fractionation, that of binary mixtures, has naturally received most attention. Although mixtures in modern practice are usually more complex, the study of binary systems has revealed a number of principles which are capable of general application.

Sorel[1] suggested a method of calculation, using as a basis an ideal column in which the vapor and liquid on each (theoretical) plate were assumed to be in complete equilibrium. This algebraic method, like the graphical methods of Ponchon[2] and Savarit[5], took into account the variations in reflux through the column due to the

*Index numbers refer to items in bibliography.

changes in temperature from plate to plate and the differences in latent heat and heat of mixing. Other graphical procedures have been proposed, principally by McCabe and Thiele[6], and by Fouché[3] and Thormann[11], which make the generally justifiable assumption of constant molal reflux. More recently, Underwood[16] has suggested an analytical method of value in the ranges of composition where use of the graphical schemes becomes tedious and inaccurate.

The concept of the theoretical plate has not offered a satisfactory basis of calculation for multi-component rectification and for the fractionation of binary mixtures when the plate efficiency is low. Considering rectification as primarily a diffusional process, Murphree[7] proposed an individual plate efficiency equal to the ratio of the actual enrichment of the vapor in passing through the plate to the ideal enrichment which would be effected if the vapor rising from the plate were in equilibrium with the liquid leaving. The use of the Murphree efficiency in the graphical calculation of fractionating columns has been described by Baker and Stockhardt[15].

Although the published results of determinations of plate efficiency and of its variation with plate design, column operation, and system studied are often contradictory, the findings of certain investigators are both interesting and important with regard to the present work.

Peters[4], in the rectification of ethyl alcohol–water mixtures, found that the efficiency decreased as the concentration of the ethyl alcohol was increased. The efficiency was about the same for sieve plates and bubble-cap plates with equal depths of liquid and equal areas of slots and perforations. Shirk and Montonna[10] found that the plate efficiency with constant reflux ratio decreased almost linearly as the rate of distillation increased. When the rate of distillation remained the same, the plate efficiency increased almost linearly with the reflux ratio expressed as $L/(V-L)$. Carey, Griswold, Lewis, and McAdams[17], in considering the bubble-cap fractionation of ethyl alcohol–water mixtures, found that the efficiency increased as the submergence of the slots was increased, but was independent of the rate of distillation. Gadwa[24], investigating the rectification of several binary systems in a column whose principal dimensions were identical with those of the apparatus used in the present work, concluded that the plate efficiency was substantially independent of concentration and, so long as foaming and entrainment did not occur, was also unaffected by changes in vapor velocity. Uchida and Matsumoto[28], in rectifying mixtures of methyl alcohol and water, and ethyl alcohol and water, in a bubble-cap column, found that the plate

efficiency was essentially independent of vapor velocity, reflux ratio, and liquid composition.

Peavy and Baker[30] found that the plate efficiency was independent of reflux ratio. At low rates of distillation, the efficiency increased with vapor velocity and then remained constant over a considerable range, dropping off as entrainment became pronounced. In the rectification of mixtures of ethyl alcohol and water, and benzene and toluene, Rhodes and Slachman[31] found that the Murphree efficiency did not vary with composition and was substantially independent of the rate of distillation. Kirschbaum[18], rectifying ethyl alcohol–water mixtures in a sieve plate column, found that the plate efficiency diminished with decreasing reflux ratio, and varied with composition, reaching a maximum at about 40 mole per cent. In a more recent study of the fractionation of the same binary system in a bubble-cap column, Kirschbaum[35] indicated that the plate efficiency was independent of reflux ratio and fell off only slightly with increasing rate of distillation (in the absence of entrainment). In this case also, the Murphree efficiency varied with concentration, but the maximum was reached at about 60 mole per cent.

Important factors which might influence the performance of the individual plates and which can be determined in advance have been discussed by Keyes[34].

3. *Theoretical Considerations.*—Rectification is essentially a process of interaction between vapor and liquid phases of a given system, involving both heat and material transfer. On the one hand, the process may be considered one in which portions of the vapor, in passing upward through the column, condense in the liquid stream, liberating heat which yields equivalent quantities of vapor containing increasingly higher concentrations of the more volatile constituents. On the other hand, fractional distillation may be assumed to be primarily a diffusional process, similar to absorption and extraction. The material transfer involves, in the simplest case of a binary mixture, the diffusion of the more volatile constituent into the vapor stream and of the less volatile component into the liquid stream. It seems probable, however, that the resolution of the problem into one or other of these basic concepts is unnecessary. The correlations of Chilton and Colburn[20a] have indicated that those factors which govern material transfer in diffusional processes should have a similar control over heat transfer in like systems. These conclusions are borne out for bubble-cap fractionation, in some measure,

by Carey's investigation of the "temperature efficiency"[23] and its relation to the Murphree plate efficiency.

Kirschbaum[18, 35], among others, has demonstrated the existence of stratified zones of vapor–liquid interaction in the operation of bubble-cap and sieve plate columns. The vapor first rises through the agitated liquid flowing across the plate and then comes into successive contact with a layer of foam or froth and a region of spray, consisting of liquid droplets thrown upward by the force of vapor passing through the bell-slots or plate perforations, or carried upward by the vapor stream. Despite the lack of definitive data, certain presumptions may be made regarding the relative importance of the zones of contact mentioned.

At low rates of distillation the upper zone of spray is absent. As the vapor velocity is increased, spray develops in increasing amounts. Unless the plate spacing is unusually large, the increase in height of this zone results in entrainment, even at moderate velocities. It may then be expected that the vapor–liquid interaction through the relatively small surface area of these droplets, under ordinary conditions of column operation, can result in only a small fraction of the total material transfer.

Carey, Griswold, Lewis, and McAdams[17], and Robinson and Gilliland[37a] have suggested that rectification in plate columns is primarily a result of the interaction between the vapor bubbles and the liquid through which they rise. Keyes[34] and Sherwood[33e], on the other hand, have proposed that most of the interphase transfer takes place as the vapor bubble is formed and during its release in the constantly breaking surface of the liquid stream. At the moderate rates of distillation commonly used in practice, the line of demarcation between the body of agitated liquid on a plate and the foam above it is indefinite, and frequently absent in sieve plate fractionation. In either case the process is one of material transfer by diffusion through phase boundaries and should be subject to the analysis applied to liquid–gas absorption.

Nomenclature

In the theoretical discussion the following nomenclature will be used:

a = area of vapor–liquid contact per mole vapor or liquid, sq. cm.

c_1, c_2 = constants in linear equations

D = diffusivity, cm.^{2}/sec.

E = local or point efficiency in terms of vapor compositions
E_o = overall Murphree efficiency in terms of vapor compositions
E_x = local plate efficiency in terms of liquid compositions
E_{ox} = overall Murphree efficiency in terms of liquid compositions
K = coefficient of mass transfer, g. moles/(sq. cm.) (sec.)
L = molal quantity of liquid reflux (referred to V)
m = slope of vapor–liquid equilibrium curve, dy^*/dx
N = molal rate of material transfer, g. moles/(sq. cm.) (sec.)
p = partial pressure of diffusing component in vapor phase, atm.
P = total pressure, atm.
R = reflux ratio, L/V or L_θ/V_θ
R' = gas constant, (cc.) (atm.)/(g. mole) (deg. K.)
T = absolute temperature, deg. K.
V = molal quantity of vapor used as a basis of calculation
w = distance along plate in direction of liquid flow, cm.
W = total length of liquid path on plate, cm.
x = composition of liquid, mole fraction of diffusing or volatile component
x^* = composition of liquid in equilibrium with vapor leaving, mole fraction
y = composition of vapor, mole fraction of diffusing or volatile component
Y = average composition of mixed vapors rising from plate, mole fraction
y^* = composition of vapor in equilibrium with liquid leaving, mole fraction
z = thickness of vapor or liquid film, cm.
θ = time of vapor–liquid contact, sec.

Subscripts

i = at vapor–liquid interface
L = per mole of liquid or in terms of liquid concentrations
n = plate under consideration
$(n + 1)$ = plate next above n-th plate
$(n - 1)$ = plate next below n-th plate
o = overall (Murphree plate efficiency)
V = per mole vapor or in terms of vapor concentrations
x = in terms of liquid compositions (plate efficiency)
θ = per unit time

Murphree Plate Efficiency

The derivation of the Murphree plate efficiency[7] may be considered a development of the diffusional concepts later outlined by Lewis and Chang[12], and Kirschbaum[22]. For purposes of simplified discussion, it is well to confine attention to a single step of continuous rectification, such as may exist on a bubble-cap or sieve plate operating under steady conditions. The mixing of the liquid on the plate may be considered sufficiently complete, so that the differences in concentration from point to point in the liquid stream are negligible.

If, as Murphree has suggested[7], the solubility of the vapors in the corresponding liquid is high, which is true in most cases of commercial rectification, and, hence, the liquid-film resistance is low, the rate of material transfer may be expressed as[33a, d]

$$N = \left(\frac{D_V P}{R' T z_V}\right)\left(\frac{p_i - p_V}{P}\right) = K_V(y^* - y) \tag{1}$$

By a rate balance through the plate,

$$V\frac{dy}{d\theta} = K_V a_V V(y^* - y).$$

Or, on integration,

$$\int_{y_{n-1}}^{y_n} \frac{dy}{y^* - y} = K_V a_V \theta$$

whence

$$\frac{y_n^* - y_n}{y_n^* - y_{n-1}} = e^{-K_V a_V \theta}.$$

From the definition of the Murphree plate efficiency,

$$E = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \tag{2}$$

it follows that

$$E = 1 - e^{-K_V a_V \theta}. \tag{3}$$

Certain preliminary and reasonable conclusions are suggested by Equation (3). The plate efficiency should increase with increased area and time of vapor–liquid contact, and with an increased value

of the overall coefficient of material transfer K_V. As Sherwood[33c] has pointed out, the term $D_V P/z_V$ is independent of the total pressure P. Moreover, the diffusivity D varies approximately as $T^{3/2}$. The efficiency may accordingly be expected to increase with the diffusivity and, to a lesser degree, with the temperature T, but should decrease with increased values of vapor-film thickness z_V.

If the liquid film is of consequence, as Furnas and Taylor[42] have suggested for the case of packed-column fractionation, the rate equation may take the form similar to that shown by Sherwood[33d]

$$N = K_L(x - x^*). \tag{4}$$

For small changes of composition across a plate the equilibrium curve may be approximated by a straight line over the composition range involved.

From Fig. 1,

$$\frac{dy^*}{dx} = \frac{y^* - y}{x - x^*} = m.$$

Hence

$$V\frac{dy}{d\theta} = \frac{K_L}{m} a_V V(y^* - y)$$

and

$$\int_{y_{n-1}}^{y_n} \frac{dy}{y^* - y} = \frac{K_L}{m} a_V \theta$$

whence

$$\frac{y_n^* - y_n}{y_n^* - y_{n-1}} = e^{-\frac{K_L}{m} a_V \theta}$$

and

$$E = 1 - e^{-\frac{K_L}{m} a_V \theta}. \tag{5}$$

Under these conditions the plate efficiency should be affected by changes in time and area of liquid–vapor interaction to the same degree as before. If the resistance of the liquid film is important, the overall coefficient of material transfer based on liquid compositions, K_L, is a function of D_L/z_L, and the efficiency should be influenced by temperature to a greater extent than in the previous case. Moreover, the efficiency should be a function of liquid composition in that it should increase with decreased values of m, the slope of the equilibrium curve.

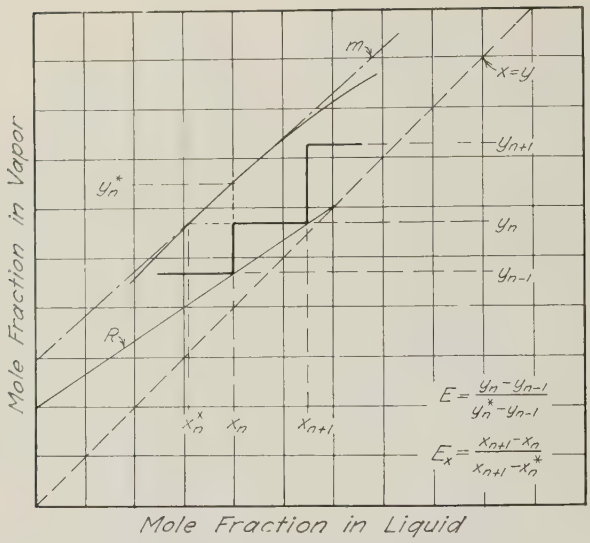


FIG. 1. RELATIONSHIP BETWEEN E AND E_x

Robinson and Gilliland[37b] have suggested that, if the main resistance to mass transfer lies in the liquid film, an equation of the type

$$E_x = \frac{x_{n+1} - x_n}{x_{n+1} - x_n^*} \tag{6}$$

similar to the plate efficiency based on vapor enrichment, is a more suitable form. If, from the form of this equation, a derivation analogous to that of Murphree is inferred, it may take the following form:

$$L\frac{dx}{d\theta} = K_L a_L L(x - x^*)$$

and, noting that $a_L L = a_V V$, or $a_L = \frac{a_V}{R}$

$$\int_{x_n}^{x_{n+1}} \frac{dx}{x - x^*} = K_L a_L \theta = \frac{K_L}{R} a_V \theta$$

whence

$$\frac{x_n - x_n^*}{x_{n+1} - x_n^*} = e^{-\frac{K_L}{R} a_V \theta}$$

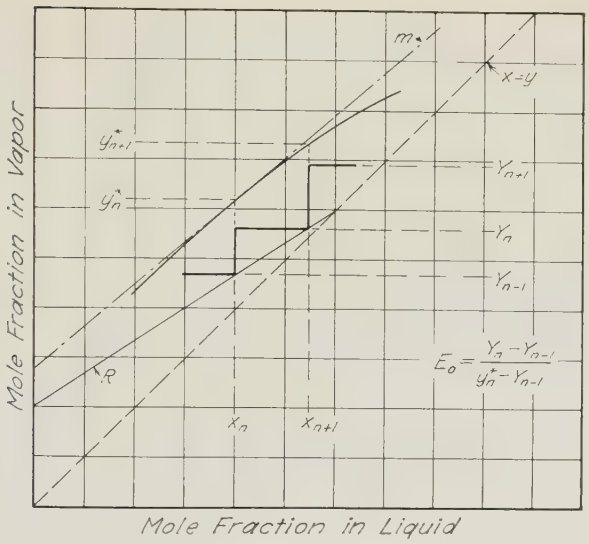


FIG. 2. RELATIONSHIP BETWEEN E AND E_o

and, since

$$E_x = \frac{x_{n+1} - x_n}{x_{n+1} - x_n^*}$$

$$E_x = 1 - e^{-\frac{K_L}{R} a_V \theta}.$$

However, the primary assumption of liquid composition x, as a plate variable, is clearly incompatible with the Murphree derivation[7], so that the equations given above do not apply. If an expression for plate efficiency in terms of the overall change in liquid composition from plate to plate is desired, resort may be had to the relationships evident in Fig. 2.

It is seen that

$$\frac{dy^*}{dx} = \frac{y_n^* - y_n}{x_n - x_n^*} = m$$

and

$$\frac{y_n - y_{n-1}}{x_{n+1} - x_n} = R.$$

If, as defined,

$$E = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}}$$

and

$$E_x = \frac{x_{n+1} - x_n}{x_{n+1} - x_n^*}$$

then

$$E_x = \frac{x_{n+1} - x_n}{(x_{n+1} - x_n) + (x_n - x_n^*)} = \frac{\dfrac{(y_n - y_{n-1})}{R}}{\dfrac{(y_n - y_{n-1})}{R} + \dfrac{(y_n^* - y_n)}{m}}.$$

Multiplying by R, and dividing by $(y_n^* - y_{n-1})$,

$$E_x = \frac{E}{E + \dfrac{R}{m}\dfrac{y_n^* - y_n}{y_n^* - y_{n-1}}}$$

$$= \frac{E}{E + \dfrac{R}{m}\left[\dfrac{y_n^* - y_{n-1}}{y_n^* - y_{n-1}} - \dfrac{y_n - y_{n-1}}{y_n^* - y_{n-1}}\right]}$$

or

$$E_x = \frac{E}{E + \dfrac{R}{m}(1 - E)} \tag{7}$$

$$= \frac{1 - e^{-\frac{K_L}{m}a_V\theta}}{1 + \left(\dfrac{R}{m} - 1\right)e^{-\frac{K_L}{m}a_V\theta}}.$$

Analogously,

$$E_{ox} = \frac{E_o}{E_o + \dfrac{R}{m}(1 - E_o)}. \tag{8}$$

Local Murphree Efficiency

The preceding discussion has assumed that the liquid on each plate of a rectifying column is completely mixed and that the efficiency may be based on the composition of the liquid leaving the

plate. In actual practice, and particularly in columns of commercial size, the mixing of the liquid stream flowing across the plate cannot be perfect and may often be very incomplete. As Kirschbaum and others have shown[21, 26, 29], the values of plate efficiency exceeding 100 per cent, which are often found in the operation of well-designed bubble-cap and sieve-plate columns, are to be expected. Even if the vapor–liquid interaction at each point is not ideally complete, a large portion of the vapor entering the plate must come into contact with liquid of a concentration considerably greater than that of the liquid leaving the plate. The result may often be a mixed vapor richer in the more volatile component than a vapor in theoretical equilibrium with the liquid leaving. The mean concentration of the liquid on the plate is not ordinarily the arithmetic average of the end conditions, since the rate of change in liquid composition is greater during the earlier part of the flow than that near the exit from the plate[26].

Lewis[27] has suggested a mathematical relationship between the overall Murphree efficiency, as customarily defined by the plate end conditions, and the local or point efficiency. When each plate contains only one bubble-cap it may reasonably be assumed that the vapor entering is of uniform composition (cf. Lewis' Case I). In the special case, making possible a simple analytical treatment, the liquid is assumed to flow across the plate in uniform streamlines with no mixing whatever, and the vapor to rise normal to the direction of liquid flow. Under fixed conditions of reflux ratio, heat input, etc., the liquid rate L across a plate and the vapor rate V up the column exhibit a definite relation to each other. The local efficiency $E = (y - Y_{n-1})/(y^* - Y_{n-1})$ is assumed constant over the plate, while the equilibrium curve and operating line are straight lines of slopes m and R, respectively, over the short range of compositions involved.

If a differential section dw of a plate n of unit width and length W is considered, at any point of distance w from the point of liquid entrance, a material balance at steady state, suggested by Sherwood and Reed[39], results in

$$L_\theta x + V_\theta Y_{n-1} \frac{dw}{W} = L_\theta(x + dx) + V_\theta y \frac{dw}{W} \qquad (9)$$

whence

$$V_\theta(y - Y_{n-1}) \frac{dw}{W} = -L_\theta dx.$$

From the definition of E,

$$y - Y_{n-1} = E(y^* - Y_{n-1})$$

and

$$\frac{dy^*}{dx} = m$$

whence

$$\frac{dw}{W} = -L_\theta V_\theta \frac{dx}{y - Y_{n-1}} = -\frac{R}{E}\frac{dx}{y^* - Y_{n-1}} = -\frac{R}{mE}\frac{dy^*}{y^* - Y_{n-1}}.$$

On integration,

$$\int_{w=o}^{w=W} \frac{dw}{W} = -\frac{R}{mE}\int_{x=x_o}^{x=x_W} \frac{dy^*}{y^* - Y_{n-1}}$$

or

$$\frac{W}{W} = \frac{R}{mE}\int_{y_n^*}^{y_{n+1}^*} \frac{dy^*}{y^* - Y_{n-1}}.$$

Therefore,

$$E = \frac{R}{m} ln \frac{y_{n+1}^* - Y_{n-1}}{y_n^* - Y_{n-1}}. \tag{10}$$

Moreover, since E is constant,

$$E = \frac{y_{n+1} - Y_{n-1}}{y_{n+1}^* - Y_{n-1}} = \frac{y_n - Y_{n-1}}{y_n^* - Y_{n-1}}$$

or

$$\frac{y_{n+1}^* - Y_{n-1}}{y_n^* - Y_{n-1}} = \frac{y_{n+1} - Y_{n-1}}{y_n - Y_{n-1}}$$

whence

$$E = \frac{R}{m} ln \frac{y_{n+1} - Y_{n-1}}{y_n - Y_{n-1}}. \tag{11}$$

If, as has been assumed, the equilibrium curve and operating line are straight lines for short distances, their equations (cf. Fig. 2) may be expressed as

$$y_n^* = mx_n + c_1$$

and

$$Y_n = Rx_{n+1} + c_2.$$

From Equation (10)

$$E = \frac{R}{m} ln \frac{y^*_{n+1} - Y_{n-1}}{y_n^* - Y_{n-1}}$$

$$= \frac{R}{m} ln \frac{mx_{n+1} + c_1 - Rx_n - c_2}{mx_n + c_1 - Rx_n - c_2}$$

$$= \frac{R}{m} ln \frac{mx_{n+1} - Rx_n + c_1 - c_2}{mx_n - Rx_n + c_1 - c_2}$$

$$= \frac{R}{m} ln \left[1 + \frac{m(x_{n+1} - x_n)}{mx_n - Rx_n + c_1 - c_2} \right] \tag{12}$$

$$E_o = \frac{Y_n - Y_{n-1}}{y_n^* - Y_{n-1}}$$

$$= \frac{Rx_{n+1} + c_2 - Rx_n - c_2}{mx_n + c_1 - Rx_n - c_2}$$

$$= \frac{R(x_{n+1} - x_n)}{mx_n - Rx_n + c_1 - c_2}$$

$$= \frac{R}{m} \frac{m(x_{n+1} - x_n)}{mx_n - Rx_n + c_1 - c_2}. \tag{13}$$

Comparing Equation (12) with Equation (13)

$$E = \frac{R}{m} ln \left(1 + E_o \frac{m}{R} \right) \tag{14}$$

or

$$E_o = \frac{R}{m} (e^{E \frac{m}{R}} - 1). \tag{15}$$

It must be emphasized that neither E nor E_o may be indiscriminately applied to any practical case, and that the actual plate efficiency will ordinarily lie between the two limiting values. The overall efficiency E_o may be conveniently used in design calculations, while

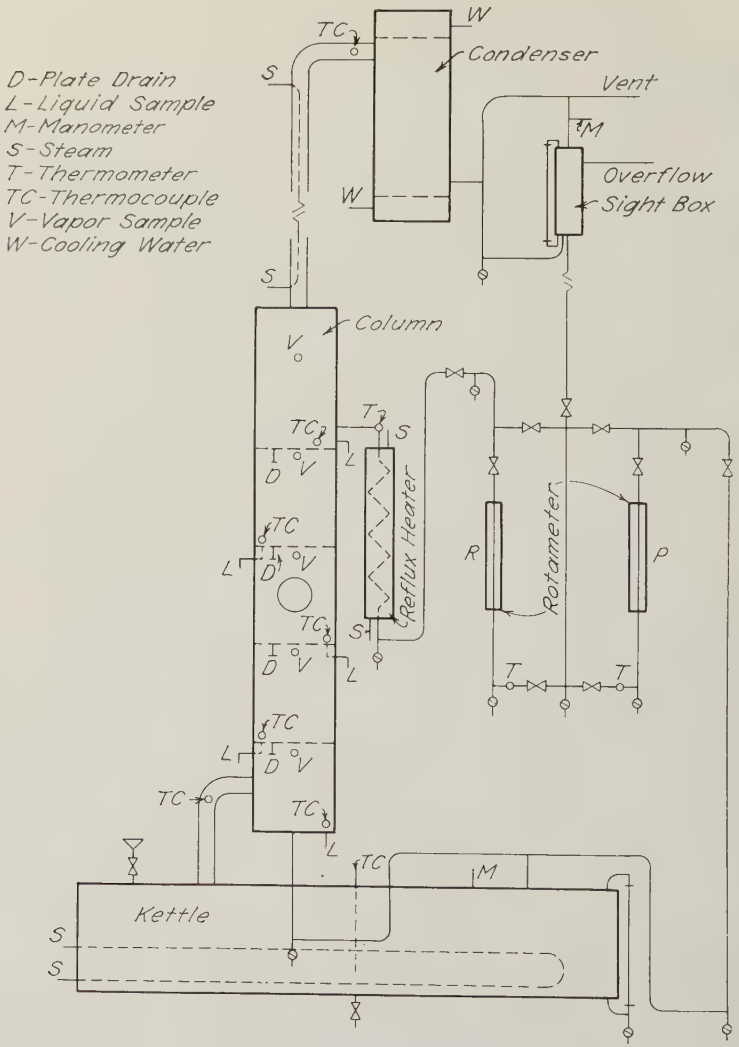


FIG. 3. APPARATUS ASSEMBLY

the local or point efficiency E is of importance in evaluating the influence of composition on plate efficiency.

4. *Acknowledgments.*—This investigation has been a part of the work of the Engineering Experiment Station, of which Dean M. L.

ENGER is the director, and of the Division of Chemical Engineering, of which Professor D. B. KEYES is the head.

The junior author did a large share of the experimental work as a basis for his thesis for the Doctor of Philosophy degree. The equipment was purchased with funds acquired from the Chemistry Department and the Graduate School.

After the thesis work was completed the junior author was permitted to continue the study for some months due to a grant from the Graduate School.

The authors are also indebted to Mr. W. M. LANGDON for his assistance in assembling the equipment and to Mr. HORACE PETTEE for his aid in the experimental work.

II. EXPERIMENTAL WORK

5. *Apparatus.*—The apparatus used in this work and shown in graphical assembly in Fig. 3, comprised the following pieces of equipment: still, four-plate rectifying column, total condenser, sight-box, reflux and product rotameters, reflux heater, and sample cooler.

The still or kettle consisted of a horizontal boiler of 10-in. standard steel pipe, 4 ft. 10 in. long. One end was closed with a welded steel disc, 9⅞ in. in diameter and ½ in. thick, while the other end was flanged and provided with a bolted, gasketed steel plate, 16 in. in diameter and ¾ in. thick. In the lower half of this removable plate were brazed three steam-heating units, each of which was a U tube of ½-in. copper tubing, approximately 4 ft. 5 in. long. The heating units were connected to a steam inlet and an outlet manifold through valves which permitted the easy use of all the heating surface or a fraction of it. The still was provided with a gage glass mounted at the welded end and a center drain at the bottom. The liquid leaving the bottom of the column through a ½-in. standard pipe U line entered the kettle at the top and near the welded end, as far from the vapor outlet as was practicable. The product portion of the condensate also entered the kettle at this point. The top of the still was provided with a filling connection, with an opening connected to a mercury manometer (essentially a safety precaution), and with a closed thermocouple well which extended below the surface of the boiling liquid. The vapor produced in the still was led to the column through a short length of 2-in. standard pipe provided with a closed thermocouple well.

Dimensions of Column

Overall inside dimensions ..... 5 in. by 9 in. by 4 ft. 11 in. high
Number of plates 4
Bottom of column to first plate ..... 10 in.
Distance between plates ..... 11 in.
Fourth plate to top of column ..... 16 in.
Cross-section of free vapor space ..... 5 in. by 5 in.

Details of Plates and Bubble-Caps

Number of caps per plate 1
Bubble-cap bell
(No. 19 std. ga.) ..... 3 in. O.D. by $2\frac{3}{4}$ in. inside height
Vapor riser or bubble-cap chimney
(No. 16 std. ga.) ..... 2 in. O.D. by 2 in.
Number of slots per cap 38
Dimensions of slot ..... $\frac{1}{8}$ in. by $\frac{5}{8}$ in.
Plate to top of slot ..... $1\frac{3}{16}$ in.
Minimum or static liquid seal above top of slot ..... $1\frac{3}{16}$ in.
Height of high dam ..... $2\frac{5}{8}$ in.
Height of low dam or overflow weir ..... 2 in.
Diameter of liquid down pipe ..... 1 in. O.D.
Area through vapor riser ..... 3.14 sq. in.
Area through annulus between vapor riser and bell ..... 3.26 sq. in.
Area through slots ..... 2.85 sq. in.
Ratio, slot area to area of free vapor space 0.114

Liquid Hold-up

From reflux rotameter to entrance to fourth plate	340 cc.
From bottom of column to kettle	160
From product rotameter to kettle	160
From condenser to sight-box	130
Remainder in piping	330
Total	1120 cc.
Hold-up in sample-wells and sampling lines:	
Liquid leaving first plate	210 cc.
Liquid leaving second plate	320
Liquid leaving third plate	330
Liquid leaving fourth plate	330
Liquid at reflux entrance	520
Total	1710 cc.

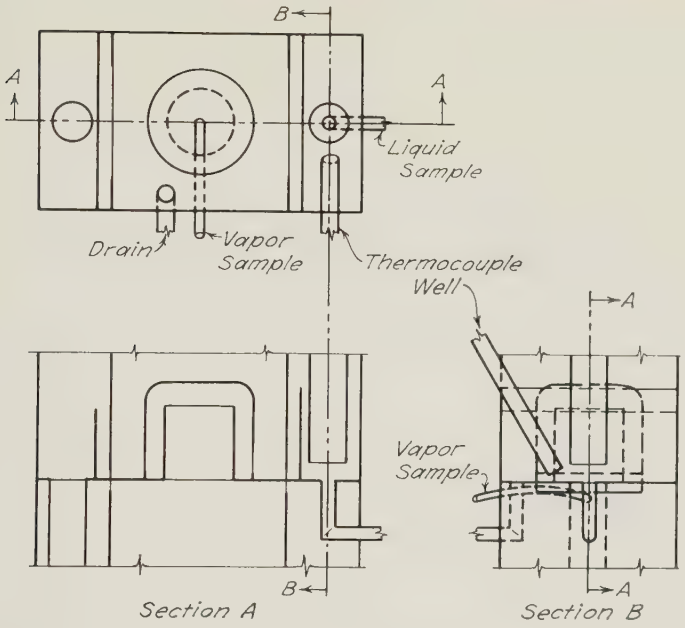


Fig. 4. Plate Details

The column, dimensions of which are given in the foregoing and the significant plate details of which are shown in Fig. 4, was constructed entirely of cold-rolled copper sheet, No. 19 standard gage. The four plates were built as separate units and mounted, by "sweating" or soldering, within the shell of the column at spacings of 11 in. The first plate was placed 10 in. above the bottom of the column, while the distance between the top and the fourth plate was 16 in. The plates were identical and arranged in the customary manner, allowing the liquid on the second and fourth plates to flow in a direction opposite to that on the first and third. The vapor from the still entered the column through an opening in the side, 5 in. below the first plate, and passed upward through the bubble-cap and vapor space of each successive plate. The vapor left the column through a 2-in. standard pipe and entered the condenser at a point $4\frac{1}{2}$ ft. above the top of the column. The vertical length of the vapor line was fitted with a centered 43-in. length of $\frac{1}{2}$-in. copper steam pipe, which served to slightly superheat the vapor and prevent partial condensation between the column and the total condenser. In order to insure uniformity of vapor flow and to prevent mixing of

the vapor and liquid phases outside the region of the bubble-caps, vertical partitions were erected between the plates. These were slotted at the top to provide for pressure equalization and at the bottom to allow for unhindered liquid flow. The vapor path was then only 5 in. by 5 in. in maximum cross-section, as compared with the overall inside dimensions of the column, 9 in. by 5 in. After passing through the reflux heater the liquid entered the column at the top plate, flowed from plate to plate, and left the column at the bottom to return to the kettle. After entering each plate through a down pipe from the plate above, the liquid passed first over a high dam which provided the necessary liquid seal or well, then under the partition, around the bubble-cap, which effected the vapor–liquid mixing, under the opposite partition, over the low dam or weir, and into the down pipe.

Each plate was provided with a drain, while liquid samples could be drawn from the wells at the bottom of each down pipe and at the reflux entrance. In order to obtain samples of vapor entering each plate and leaving the column, an open-ended tube was installed immediately below the center of each bubble-cap and at a centered point 11 in. above the top plate. To prevent the contamination of the vapor samples with droplets of liquid which might enter the sampling tubes, each tube was curved downward within the column, and its opening was fitted with a tubular screen. Each liquid well was provided with an open-ended thermocouple tube. Sight-glasses, $3\frac{5}{8}$ in. in diameter, were mounted on opposite sides of the column between the second and third plates to provide a means for observation of the distillation process and of the action of the bubble-cap.

The vertical, water-tube, total condenser consisted of an 8-in. standard steel pipe shell, 24 in. long, and was provided with 31 copper tubes, $\frac{3}{4}$ in. in outside diameter and 18 in. long, rolled into steel tube sheets or end plates. The ends of the condenser shell were closed with gasketed and bolted steel plates. The vapor inlet was fitted with an open-ended thermocouple well, and the condensate outlet was vented and connected to the sight-box through $\frac{3}{16}$-in. copper tubing.

The sight-box, to which the condensate passed before being metered, consisted of a closed cylinder of brass pipe, 4 in. in outside diameter and 10 in. long, mounted vertically at about the same level as the bottom of the condenser and directly above the rotameters, providing a fluid head of 4 ft. above the top plate. It was fitted with a gage glass, an atmospheric vent and, as safety measures, a

mercury manometer and a ¼-in. copper overflow tube which led to a reservoir. The sight-box, by providing a necessary vent and damping chamber, aided in maintaining a smooth flow of condensate and, at high rates of distillation, gave visual warning when the liquid return lines, of ⅜-in. standard pipe, were being overloaded.

The condensate, after leaving the sight-box, was separated into two streams, reflux and product. The proportioning of the streams was controlled by means of two needle valves, and the rates of flow were measured by rotameters. Thermometers were inserted in both lines to indicate the temperature of the liquid streams entering the rotameters.

After passing through a ⅜-in. standard pipe U line and immediately before entering the rectifying column at the top plate, the reflux was heated to a temperature just below its boiling point by passing upward through the copper coil (¼ in. in outside diameter and 7 ft. long when extended) of a vertically-mounted steam preheater, the shell of which consisted of a capped 20-in. length of 3-in. standard pipe. A thermometer was inserted at the top of the coil to indicate the temperature of the reflux entering the column. The product stream was led directly to the kettle after passing through a ⅜-in. standard pipe U line.

The sample cooler consisted of a rectangular, galvanized sheet steel water tank, 9 in. by 6 in. by 30 in., mounted vertically and as close as practicable to the column. Each of the vapor and liquid samples was drawn from the column and led through the cooler through a minimum length of 3/16-in. copper tubing to a vented, stoppered vial, attached to a needle petcock.

The steam required for the operation of the kettle, the reflux heater, and the vapor superheater was drawn from a high-pressure (100 lb. per sq. in.) line and reduced to suitable low pressures through steam regulators.

Each of the copper-constantan thermocouples which were installed to measure the temperature of the liquid in the kettle, entering the top plate and leaving each of the four plates, and the temperature of the vapor entering the column and entering the condenser, was connected through a switchboard to a common ice-water cold junction and a portable potentiometer.

The entire apparatus was well insulated to prevent heat losses and to make the experiments less sensitive to variations in external conditions. The kettle was covered with 2-in. magnesia pipe lagging, and the column was completely insulated (except for the sight-glasses) with 2-in. magnesia blocks. The latter precaution was es-

sential to insure the constancy of the reflux ratio throughout the column—unchanged by partial condensation from plate to plate. The reflux heater, the vapor line from column to condenser, and all the pipe lines which carried steam, vapor, or hot liquid were lagged with standard 1-in. magnesia covering.

6. *Procedure.* —Three sets of runs were made, covering almost the entire composition range of the binary system, ethyl alcohol–water. Each set of runs comprised three groups of reflux ratios (reflux to total vapor): 1 : 1, 2 : 3, and 1 : 2. The number of runs in the groups $L/V = 1$ varied from 11 to 15, while the groups $L/V = \frac{2}{3}$ and $\frac{1}{2}$, contained 7 to 15 individual runs. In general, the first run of each group was made at the lowest possible rate of distillation, and each succeeding run was made at a greater rate until the capacity of the liquid return lines was reached. In this way the superficial vapor velocity was varied, in fairly regular increments, from 0.2 to 3.0 ft. per sec. (based on the maximum cross-section of the vapor path through the column—25 sq. in.). An itemized list of the recorded operating data follows.

Recorded Data

1. Time at start of steady state operation
2. Time at start of sampling period
3. Temperatures at start of sampling period
   - (a) Liquid in kettle
   - (b) Vapor entering column
   - (c) Liquid leaving first (bottom) plate
   - (d) Liquid leaving second plate
   - (e) Liquid leaving third plate
   - (f) Liquid leaving fourth (top) plate
   - (g) Liquid on top plate
   - (h) Vapor entering condenser
4. Readings of reflux and product rotameters
5. Temperature of condensate entering rotameters
6. Description of bubble-cap action
7. Barometric pressure
8. Temperatures at end of sampling period (as in item 3)
9. Time at end of sampling period
10. Number of pycnometer for each vapor or liquid sample analyzed
    - (a) Sample of liquid leaving first plate
    - (b) Sample of liquid leaving second plate

(c) Sample of liquid leaving third plate
(d) Sample of liquid leaving fourth plate
(e) Sample of liquid entering fourth plate
(f) Sample of liquid condensate
(g) Sample of vapor entering first plate
(h) Sample of vapor leaving first plate
(i) Sample of vapor leaving second plate
(j) Sample of vapor leaving third plate
(k) Sample of vapor leaving fourth plate

11. Gross weights of filled pycnometers

In preparation for each set of runs, the apparatus was drained of the solution previously used, and the kettle was refilled with 10 to 12 gallons of a mixture of the desired composition. Steam was admitted to one or more of the heating units of the still. When distillation had begun, the steam-pressure reducing and regulating valves were adjusted to give the desired rate, and the flow of condenser water was set to maintain the condensate temperature as close as possible to 25 deg. C., the calibration temperature of the rotameters. Steam was admitted to the superheater in the vapor line from column to condenser and to the reflux preheater, which heated the reflux stream to within one or two degrees of its boiling point. The apparatus was operated for a period of two or more hours, during which only minor adjustments were required to maintain the operation under steady conditions, as indicated by the sight-box, rotameters, thermometers, thermocouples, manometers, steam-pressure gages, and sight-glasses. The rectification process was continued at a steady state for a minimum period of four hours, a time which preliminary experiments had shown to be sufficient to insure invariant conditions even at the lowest rates of distillation. At this point temperatures were recorded, and the operation was continued throughout the sampling period of from 1½ to 2 hours; at the end of this period temperatures were read again to check on the constancy of the operation. In general, the two sets of temperatures showed no regular or significant differences. In every case the temperature of the vapor entering the column was equal to or slightly lower than that of the kettle charge, while the temperature of the vapor entering the condenser was always two or three degrees higher than that of the liquid on the top plate—indicating the absence of partial condensation in the insulated vapor line.

Five samples, in all, of liquid entering the column at the top plate and leaving each of the four plates were taken simultaneously

with five samples, in all, of vapor entering the bubble-caps of the four plates and leaving the column above the top plate. Not more than 125 ml. (25 cc. per sample) of condensed vapor was withdrawn from the column during the sampling period, at a maximum rate of 0.3 ml. per min., while approximately 225 ml. of liquid samples (45 ml. per sample), at an average rate of 0.5 ml. per min., was taken. Only the last 8 to 10 ml. of each sample was saved for the determination of the composition of the liquid and vapor streams at the several selected points. The previously collected "wash" samples served to purge the sample tubes and lines, and were set aside, later to be returned to the kettle, together with the analyzed portions. When the sampling had been completed, the steam was shut off, and the column and kettle were opened to the air, in order to break the vacuum which followed the cooling and condensation of the vapors in the apparatus, and which might cause the collapse of the straight-walled column. The last sample taken was that of the condensate and was withdrawn from any convenient petcock in the return lines. The apparatus could now be prepared for the next run, and the samples analyzed. Sometime during the course of each run a reading of the barometric pressure was made, as required for the calculation of vapor rates. Whenever the interval between runs was long enough to allow the still charge to cool, a sample of liquid was withdrawn through the gage-glass petcock and its density determined by hydrometry. Since this sample was always contaminated with rust and could not be analyzed accurately, it served merely as a check on the slow change of kettle composition with increasing rates of distillation.

The compositions of the several samples were determined by the pycnometric method described by Langdon[36]. The necessary data for the densities of water and ethyl alcohol-water mixtures were found in Perry's *Chemical Engineers' Handbook*[23], while the vapor–liquid equilibrium data of Bergström as given by Hausbrand[9], were used in determining plate efficiencies. A re-tabulation of the data mentioned is to be found in the Appendix.

7. *Results.*—The principal results of this investigation are summarized in Table 1. Liquid and vapor compositions x_n and Y_n^s, as observed, were plotted as functions of vapor rate, and values were taken for tabulation by graphical interpolation at superficial vapor velocities (through the free vapor space, 25 sq. in. in cross-section) of 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, and 2.6 ft. per sec.

Although the plate efficiencies[7], as derived from Equations (3), (5), (7), (8), and (14), assumed constant molal reflux throughout the

Table 1
Summary of Experimental Results

Nomenclature

E = local plate efficiency in terms of vapor compositions, $R/m[ln(1 + E_o m/R)]$, per cent
E_o = overall Murphree efficiency in terms of vapor compositions, $(Y_n - Y_{n-1})/(y_n^* - Y_{n-1})$, per cent
E_{ox} = overall plate efficiency in terms of liquid compositions, $(x_{n+1} - x_n)/(x_{n+1} - x_n^*)$, per cent
L_R = composition of condensate sample (reflux), mole per cent ethyl alcohol
m = slope of vapor–liquid equilibrium curve dy^*/dx (cf. Fig. 5)
n = number of plate from bottom of column
R = reflux ratio at top plate $(L/V)_1$
u = superficial vapor velocity through free space, ft. per sec.
V_K = composition of vapor entering first (bottom) plate, mole per cent alcohol
x = composition of liquid leaving plate, mole per cent alcohol
x^* = composition of liquid in equilibrium with Y^c, mole per cent alcohol (cf. Table 5)
Y^s = composition of mixed vapors leaving plate, as sampled, mole per cent alcohol
Y^c = composition of mixed vapors leaving plate, corrected, mole per cent alcohol (cf. Fig. 5)
y^* = composition of vapor in equilibrium with x, mole per cent alcohol (cf. Table 5)

Subscripts

$a.m.$ = arithmetic mean of compositions of liquid entering and leaving plate (for calculation of E)
n = plate under consideration
$(n + 1)$ = plate next above nth plate
$(n - 1)$ = plate next below nth plate
o = overall (plate efficiency)
x = in terms of liquid compositions (plate efficiency)

u	n	x_n	y_n^*	Y_n^s	Y_n^c	x_n^*	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n^* - Y_{n-1}$	$x_{n+1} - x_n^*$	E_o	$x_{a.m.}$	m	R	E	E_{ox}
High Concentration Range; Total Reflux $L/V = 1$; Runs A (1-15)																
0.2	L_R	81.90														
	4	80.83	82.36	82.10	81.90	80.21	1.32	1.07	1.78	1.69	74	81.3	0.70	1	59	63
	3	79.16	81.15	80.69	80.58	78.38	1.43	1.67	2.00	2.45	71	80.0	0.70		58	68
	2	77.05	79.62	79.26	79.15	76.40	2.28	2.11	2.75	2.76	83	78.1	0.67		66	76
	1	73.62	77.16	77.01	76.87	73.16	3.29	3.43	3.58	3.89	92	75.3	0.65		72	88
	V_K			73.77	73.58											
0.6	L_R	81.67														
	4	80.50	82.12	81.84	81.67	79.89	1.33	1.17	1.78	1.78	75	81.1	0.70	1	60	66
	3	78.79	80.88	80.44	80.34	78.04	1.56	1.71	2.10	2.46	74	79.7	0.70		59	70
	2	76.58	79.28	78.90	78.78	75.89	2.34	2.21	2.84	2.90	82	77.8	0.67		65	76
	1	73.13	76.85	76.60	76.44	72.49	3.36	3.45	3.77	4.09	89	74.8	0.64		70	84
	V_K			73.27	73.08											

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	y_n*	Y_n[a]	Y_n[c]	x_n*	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	y_n* $- Y_{n-1}$	$x_{n+1} - x_n$*	E_o	$x_{a.m.}$	m	R	E	E_{ox}
1.0	L_R	81.44														
	4	80.20	81.90	81.59	81.44	79.57	1.35	1.24	1.81	1.87	75	80.8	0.70	1	60	66
	3	78.45	80.63	80.20	80.09	77.70	1.64	1.75	2.18	2.50	75	79.3	0.70		60	70
	2	76.13	78.95	78.57	78.45	75.45	2.41	2.32	2.91	3.00	83	77.3	0.67		66	77
	1	72.65	76.55	76.20	76.04	71.86	3.46	3.48	3.97	4.27	87	74.4	0.64		69	82
	V_K			72.77	72.58											
1.4	L_R	81.22														
	4	79.91	81.69	81.37	81.22	79.26	1.35	1.31	1.82	1.96	74	80.6	0.70	1	59	67
	3	78.11	80.39	79.99	79.97	77.40	1.76	1.80	2.28	2.51	77	79.0	0.69		62	72
	2	75.67	78.61	78.24	78.11	74.99	2.47	2.44	2.97	3.12	83	76.8	0.67		66	78
	1	72.18	76.25	75.80	75.64	71.23	3.58	3.49	4.19	4.44	85	73.9	0.64		68	79
	V_K			72.26	72.06											
1.8	L_R	81.00														
	4	79.63	81.48	81.12	81.00	78.96	1.35	1.37	1.83	2.04	74	80.3	0.70	1	59	67
	3	77.77	80.14	79.76	79.65	77.10	1.85	1.86	2.34	2.53	79	78.7	0.68		63	73
	2	75.21	78.27	77.93	77.80	74.56	2.57	2.56	3.04	3.21	84	76.4	0.67		67	80
	1	71.69	75.93	75.40	75.23	70.59	3.68	3.52	4.38	4.62	84	73.4	0.64		67	76
	V_K			71.75	71.55											
Medium Concentration Range; Total Reflux $L/V = 1$; Runs C (1-13)																
0.2	L_R	78.11														
	4	75.47	78.47	78.25	78.11	74.99	2.85	2.64	3.21	3.12	89	76.8	0.67	1	70	85
	3	71.71	75.94	75.41	75.26	70.64	3.27	3.76	3.95	4.83	83	73.7	0.64		66	78
	2	65.64	72.48	72.19	71.99	64.82	6.3	6.07	6.8	6.89	93	68.7	0.61		73	88
	1	54.72	66.71	66.14	65.7	52.5	10.6	10.92	11.6	13.1	91	60.2	0.50		75	83
	V_K			55.97	55.1											
0.6	L_R	77.82														
	4	75.20	78.27	77.99	77.82	74.58	2.82	2.62	3.27	3.24	86	76.5	0.67	1	68	81
	3	71.41	75.75	75.17	75.00	70.22	3.43	3.79	4.18	4.98	82	73.3	0.64		66	76
	2	65.26	72.26	71.78	71.57	64.18	6.2	6.15	6.9	7.23	90	68.3	0.60		72	85
	1	54.38	66.58	65.78	65.4	51.9	10.9	10.88	12.1	13.4	90	59.8	0.50		74	81
	V_K			55.41	54.5											
1.0	L_R	77.52														
	4	74.96	78.09	77.74	77.52	74.17	2.76	2.56	3.33	3.35	83	76.2	0.66	1	66	76
	3	71.12	75.57	74.93	74.76	69.85	3.59	3.84	4.40	5.11	82	73.0	0.64		66	75
	2	64.87	72.02	71.38	71.17	63.50	6.2	6.25	7.0	7.62	88	68.0	0.60		71	82
	1	54.06	66.46	65.41	65.0	51.0	11.0	10.81	12.5	13.9	88	59.5	0.50		73	78
	V_K			54.87	54.0											

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	y_n^*	Y_n^*	Y_n^c	x_n^*	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n^* - Y_{n-1}$	$x_{n+1} - x_n^*$	E_o	$x_{a.m.}$	m	R	E	E_{ox}
1.4	L_R	77.27														
	4	74.72	77.92	77.51	77.27	73.79	2.74	2.55	3.39	3.48	81	76.0	0.66	1	65	73
	3	70.87	75.41	74.71	74.53	69.50	3.75	3.85	4.63	5.22	81	72.8	0.63		65	74
	2	64.49	71.77	70.99	70.78	62.81	6.2	6.38	7.2	8.06	86	67.7	0.60		69	79
	1	53.71	66.30	65.07	64.6	50.0	11.3	10.78	13.0	14.5	67	59.1	0.49		73	74
	V_K			54.33	53.3											
1.8	L_R	77.00														
	4	74.49	77.75	77.29	77.00	73.37	2.68	2.51	3.43	3.63	78	75.7	0.66	1	63	69
	3	70.60	75.24	74.49	74.32	69.18	3.94	3.89	4.86	5.31	81	72.6	0.63		65	73
	2	64.11	71.52	70.60	70.38	62.11	6.2	6.49	7.3	8.49	84	67.4	0.60		68	77
	1	53.38	66.14	64.72	64.2	49.4	11.4	10.73	13.3	14.7	86	58.8	0.48		72	73
	V_K			53.79	52.8											
Low Concentration Range; Total Reflux $L/V = 1$; Runs B (1-11)																
0.2	L_R	76.84														
	4	73.32	76.97	76.74	76.84	73.11	3.76	3.52	3.89	3.73	97	75.1	0.64	1	75	94
	3	67.62	73.47	73.27	73.08	66.87	5.9	5.70	6.3	6.45	94	70.4	0.61		74	88
	2	54.6	66.7	67.63	67.2	55.9	11.0	13.0	10.5	11.7	105	61.1	0.51		84	111
	1	22.6	53.8	57.0	56.2	27.9	31.8	32.0	29.4	26.7	108	38.6	0.41		89	120
	V_K			26.8	24.4											
0.6	L_R	74.66														
	4	70.47	75.16	74.71	74.66	69.70	4.41	4.19	4.91	4.96	90	72.6	0.63	1	71	84
	3	63.85	71.37	70.48	70.25	61.87	6.7	6.62	7.8	8.60	86	67.2	0.60		69	77
	2	47.5	63.5	64.07	63.6	47.8	13.7	16.4	13.6	16.1	101	55.7	0.45		83	102
	1	17.7	51.3	51.0	49.9	15.3	32.3	29.8	33.7	32.2	96	32.6	0.40		81	93
	V_K			20.4	17.6											
1.0	L_R	73.39														
	4	68.99	74.19	73.59	73.39	67.47	4.69	4.40	5.49	5.92	85	71.2	0.62	1	68	74
	3	62.39	70.54	69.04	68.7	58.98	7.4	6.60	9.2	10.01	80	65.7	0.58		66	66
	2	43.3	61.5	61.93	61.3	42.8	14.8	19.1	15.0	19.6	99	52.9	0.42		83	97
	1	14.8	49.5	47.7	46.5	11.5	32.5	28.5	35.5	31.8	91	29.1	0.39		78	90
	V_K			16.9	14.0											
1.4	L_R	72.67														
	4	68.06	73.70	72.91	72.67	65.97	4.87	4.61	5.90	6.70	83	70.4	0.61	1	67	69
	3	61.56	70.07	68.08	67.8	57.15	8.1	6.50	10.4	10.91	78	64.8	0.57		65	60
	2	39.8	60.3	60.42	59.7	38.0	15.7	21.8	16.3	23.6	96	50.7	0.41		81	92
	1	13.1	48.2	45.4	44.0	9.7	32.5	26.7	36.7	30.1	89	26.5	0.42		76	89
	V_K			14.6	11.5											

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	$y_n{}^*$	$Y_n{}^b$	$Y_n{}^c$	$x_n{}^*$	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n{}^* - Y_{n-1}$	$x_{n+1} - x_n{}^*$	E_o	$x_{a.m.}$	m	R	E	E_{oz}
1.8	L_R	72.36														
	4	67.39	73.35	72.52	72.36	65.43	5.36	4.97	6.35	6.93	84	69.9	0.61	1	68	72
	3	61.12	69.83	67.37	67.0	55.43	8.2	6.27	11.0	11.96	74	64.3	0.56		62	52
	2	36.7	59.3	59.48	58.8	35.3	16.4	24.4	16.9	25.8	97	48.9	0.40		82	95
	1	12.3	47.4	43.8	42.4	8.8	32.4	24.4	37.4	27.9	87	24.5	0.44		74	87
	V_K			13.1	10.0											
		High Concentration Range; Reflux Ratio $L/V = \frac{2}{3}$; Runs A (32-38)														
0.6	L_R	79.06														
	4	76.95	79.54	79.20	79.06	76.28	1.73	2.11	2.21	2.78	78			0.66		76
	3	74.60	77.83	77.48	77.33	73.89	1.25	2.35	1.75	3.06	71	75.8	0.65		54	77
	2	72.31	76.33	76.23	76.08	71.92	1.55	2.29	1.80	2.68	86	73.5	0.64		62	86
	1	69.62	74.61	74.70	74.53	69.50	1.59	2.69	1.67	2.81	95	71.0	0.62		68	96
	V_K			73.12	72.94											
1.0	L_R	79.02														
	4	76.89	79.50	79.20	79.02	76.22	1.69	2.13	2.17	2.80	78			0.67		76
	3	74.57	77.81	77.48	77.33	73.89	1.27	2.32	1.75	3.00	73	75.7	0.65		55	77
	2	72.33	76.34	76.21	76.06	71.89	1.58	2.24	1.86	2.68	85	73.5	0.64		62	84
	1	69.68	74.65	74.66	74.48	69.42	1.64	2.65	1.81	2.91	91	71.0	0.62		66	91
	V_K			73.02	72.84											
1.4	L_R	79.00														
	4	76.84	79.46	79.20	79.00	76.19	1.72	2.16	2.18	2.81	79			0.67		77
	3	74.54	77.79	77.43	77.28	73.81	1.26	2.30	1.77	3.03	71	75.7	0.65		54	76
	2	72.34	76.35	76.18	76.02	71.83	1.58	2.20	1.91	2.71	83	73.4	0.64		61	81
	1	69.74	74.69	74.60	74.44	69.36	1.72	2.60	1.97	2.98	87	71.0	0.62		64	87
	V_K			72.92	72.72											
1.8	L_R	78.99														
	4	76.80	79.44	79.20	78.99	76.18	1.73	2.19	2.18	2.81	79			0.68		78
	3	74.53	77.78	77.40	77.26	73.78	1.26	2.27	1.78	3.02	71	75.7	0.65		54	75
	2	72.37	76.37	76.17	76.00	71.80	1.60	2.16	1.97	2.73	81	73.5	0.64		60	79
	1	69.80	74.73	74.57	74.40	69.30	1.77	2.57	2.10	3.07	84	71.1	0.62		62	84
	V_K			72.81	72.63											
2.2	L_R	78.99														
	4	76.78	79.42	79.20	78.99	76.18	1.73	2.21	2.16	2.81	80			0.68		79
	3	74.51	77.77	77.40	77.26	73.78	1.26	2.27	1.77	3.00	71	75.7	0.65		54	76
	2	72.40	76.39	76.17	76.00	71.80	1.65	2.11	2.04	2.71	81	73.5	0.64		60	78
	1	69.88	74.78	74.51	74.35	69.23	1.82	2.52	2.25	3.17	81	71.1	0.62		61	80
	V_K			72.72	72.53											

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	$y_n{}^*$	$Y_n{}^b$	$Y_n{}^c$	$x_n{}^*$	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n{}^* - Y_{n-1}$	$x_{n+1} - x_n{}^*$	E_o	$x_{a.m.}$	m	R	E	E_{ox}
Medium Concentration Range; Reflux Ratio L/V = ⅔; Runs C (14-20)																
0.6	L_R	73.76														
	4	69.19	74.33	73.81	73.76	68.17	3.48	4.57	4.05	5.59	86			0.66		82
	3	63.40	71.11	70.49	70.28	61.93	4.1	5.79	4.9	7.26	84	66.3	0.59		63	80
	2	55.53	67.04	66.63	66.2	53.5	5.2	7.87	6.0	9.9	87	59.5	0.52		66	80
	1	43.96	61.78	61.61	61.0	42.1	7.6	11.57	8.4	13.5	90	49.8	0.40		72	86
	V_K			54.41	53.4											
1.0	L_R	73.58														
	4	68.94	74.17	73.69	73.58	67.83	3.41	4.64	4.00	5.75	85			0.67		81
	3	63.10	70.95	70.38	70.17	61.73	4.0	5.84	4.8	7.21	83	66.0	0.58		62	81
	2	55.20	66.90	66.55	66.2	53.5	5.3	7.90	6.0	9.6	88	59.2	0.49		68	82
	1	43.63	61.65	61.54	60.9	41.4	7.8	11.57	8.6	13.8	91	49.4	0.40		73	84
	V_K			54.09	53.1											
1.4	L_R	73.40														
	4	68.70	74.04	73.57	73.40	67.49	3.35	4.70	3.99	5.91	84			0.68		79
	3	62.79	70.77	70.27	70.05	61.52	4.0	5.91	4.7	7.18	85	65.8	0.58		64	82
	2	54.87	66.76	66.47	66.1	53.3	5.2	7.92	5.9	9.5	88	58.8	0.49		68	84
	1	43.32	61.52	61.48	60.9	41.4	8.1	11.55	8.7	13.5	93	49.1	0.40		74	86
	V_K			53.77	52.8											
1.8	L_R	73.22														
	4	68.46	73.91	73.45	73.22	67.15	3.3	4.76	4.0	6.07	82			0.68		79
	3	62.49	70.60	70.15	69.9	61.3	3.9	5.97	4.6	7.2	85	65.5	0.58		64	83
	2	54.51	66.63	66.38	66.0	53.1	5.2	7.98	5.8	9.4	90	58.5	0.49		69	85
	1	43.00	61.39	61.41	60.8	40.9	8.4	11.51	9.0	13.6	93	48.8	0.40		74	85
	V_K			53.42	52.4											
2.2	L_R	73.03														
	4	68.21	73.78	73.32	73.03	66.76	3.2	4.82	4.0	6.27	80			0.68		77
	3	62.19	70.43	70.03	69.8	61.1	3.9	6.02	4.5	7.1	87	65.2	0.58		65	84
	2	54.18	66.51	66.29	65.9	52.9	5.2	8.01	5.8	9.3	90	58.2	0.48		70	86
	1	42.69	61.26	61.34	60.7	40.6	8.6	11.49	9.2	13.5	93	48.4	0.39		75	85
	V_K			53.09	52.1											
2.6	L_R	72.87														
	4	67.98	73.66	73.20	72.87	66.40	3.2	4.89	4.0	6.47	80			0.68		76
	3	61.89	70.26	69.93	69.7	60.9	3.9	6.09	4.5	7.1	87	64.9	0.57		65	86
	2	53.83	66.36	66.19	65.8	52.7	5.1	8.06	5.7	9.2	89	57.9	0.48		69	88
	1	42.37	61.13	61.28	60.7	40.6	9.0	11.46	9.4	13.2	96	48.1	0.39		77	87
	V_K															

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	$y_n{}^*$	$Y_n{}^a$	$Y_n{}^c$	$x_n{}^*$	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n{}^* - Y_{n-1}$	$x_{n+1} - x_n{}^*$	E_o	$x_{a.m.}$	m	R	E	E_{oz}
Low Concentration Range; Reflux Ratio $L/V = \frac{2}{3}$; Runs B (22-30)																
0.6	L_R	54.54														
	4	28.49	56.41	54.92	54.54	24.2	15.4	26.05	17.3	30.3	89			0.66		86
	3	66.18	36.14	40.79	39.1	7.3	17.7	22.31	14.7	21.2	120	17.3	0.56		83	105
	2	2.87	23.2	24.00	21.4	2.6	4.2	3.31	6.0	3.6	70	4.5	3.9		28	92
	1	2.22	19.4	20.02	17.2	1.9	0.7	0.65	2.9	1.0	24	2.6	5.6		13	65
	V_K			19.28	16.5											
1.0	L_R	44.75														
	4	12.34	47.40	45.81	44.75	10.2	22.6	32.41	25.2	34.6	90			0.70		94
	3	3.02	24.0	24.67	22.2	2.7	9.2	9.32	11.0	9.6	84	7.7	2.3		40	97
	2	1.67	15.6	16.01	13.0	1.3	1.5	1.35	4.1	1.7	37	2.4	6.0		17	79
	1	1.44	13.9	14.57	11.5	1.1	0.1	0.23	2.5	0.6	4	1.6	7.3		3	38
	V_K			14.48	11.4											
1.4	L_R	43.73														
	4	11.63	46.60	45.00	43.73	9.6	22.3	32.10	25.2	34.1	88			0.70		94
	3	2.90	23.4	23.95	21.4	2.6	8.8	8.73	10.8	9.0	81	7.3	2.4		39	97
	2	1.63	15.3	15.69	12.6	1.3	1.4	1.27	4.1	1.6	34	2.3	6.1		16	79
	1	1.40	13.6	14.29	11.2	1.1	0.0	0.23	2.4	0.5	0	1.5	7.4		0	46
	V_K			14.27	11.2											
1.8	L_R	42.73														
	4	10.93	45.75	44.20	42.73	9.0	22.1	31.80	25.2	33.7	88			0.70		94
	3	2.78	22.7	23.23	20.6	2.4	8.3	8.15	10.4	8.5	80	6.9	2.5		38	96
	2	1.59	15.0	15.37	12.3	1.2	1.4	1.19	4.1	1.6	34	2.2	6.2		16	74
	1	1.38	13.5	14.02	10.9	1.1	0.0	0.21	2.6	0.5	0	1.5	7.4		0	42
	V_K			14.04	10.9											
2.2	L_R	41.71														
	4	10.21	44.67	43.41	41.71	8.5	21.8	31.50	24.8	33.2	88			0.69		95
	3	2.67	22.0	22.52	19.9	2.3	8.0	7.54	10.1	7.9	79	6.4	2.8		35	95
	2	1.55	14.7	15.02	11.9	1.2	1.2	1.12	4.0	1.5	30	2.1	6.4		14	75
	1	1.34	13.2	13.76	10.7	1.0	0.0	0.21	2.5	0.6	0	1.4	7.4		0	35
	V_K			13.83	10.7											
2.6	L_R	40.71														
	4	9.50	43.56	42.62	40.71	8.0	21.6	31.21	24.5	32.7	88			0.69		95
	3	2.56	21.4	21.81	19.1	2.2	7.5	6.94	9.8	7.3	77	6.0	2.9		34	95
	2	1.51	14.4	14.70	11.6	1.2	1.2	1.05	4.0	1.4	30	2.0	6.6		14	75
	1	1.31	13.0	13.48	10.4	1.0	...	0.20	2.5	0.5	..	1.4	7.4		0	40
	V_K			13.62	10.5											

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	y_n^*	Y_n^a	Y_n^c	x_n^*	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n^* - Y_{n-1}$	$x_{n+1} - x_n^*$	E_o	$x_{a.m.}$	m	R	E	E_{ox}
High Concentration Range; Reflux Ratio L/V = ½; Runs A (17-31)																
0.2	L_R	78.22														
	4	75.24	78.30	78.09	78.22	75.14	1.74	2.98	1.82	3.08	96			0.51		97
	3	72.77	76.62	76.63	76.48	72.55	1.17	2.47	1.31	2.69	89	74.1	0.64		60	92
	2	70.78	75.35	75.48	75.31	70.71	1.05	1.99	1.09	2.06	96	71.8	0.64		63	97
	1	68.87	74.13	74.43	74.26	69.09	1.04	1.91	0.91	1.69	114	69.8	0.61		72	113
	V_K			73.40	73.22											
0.6	L_R	77.86														
	4	74.88	78.03	77.78	77.86	74.64	1.73	2.98	1.90	3.22	91			0.50		
	3	72.37	76.37	76.29	76.13	72.00	1.12	2.51	1.36	2.88	82	73.6	0.64		56	93
	2	70.33	75.07	75.17	75.01	70.24	1.08	2.04	1.14	2.13	95	71.4	0.63		63	87
	1	68.37	73.77	74.10	73.93	68.49	1.04	1.96	0.98	1.84	106	69.4	0.61		68	96
	V_K			73.07	72.89											
1.0	L_R	77.51														
	4	74.53	77.78	77.47	77.51	74.15	1.73	2.98	2.00	3.36	86			0.50		89
	3	71.98	76.12	75.94	75.78	71.45	1.11	2.55	1.45	3.08	76	73.3	0.64		53	83
	2	69.90	74.79	74.84	74.67	69.71	1.08	2.08	1.20	2.27	90	70.9	0.62		60	91
	1	67.88	73.61	73.78	73.59	67.85	1.06	2.02	1.08	2.05	98	68.9	0.60		65	95
	V_K			72.73	72.53											
1.4	L_R	77.17														
	4	74.21	77.55	77.18	77.17	73.64	1.69	2.96	2.07	3.53	82			0.50		84
	3	71.61	75.88	75.63	75.48	70.99	1.10	2.60	1.50	3.22	73	72.9	0.64		52	81
	2	69.48	74.52	74.55	74.38	69.27	1.13	2.13	1.27	2.34	89	70.6	0.62		60	91
	1	67.39	73.35	73.43	73.25	67.21	1.05	2.09	1.15	2.27	91	68.4	0.60		61	92
	V_K			72.40	72.20											
1.8	L_R	76.83														
	4	73.88	77.32	76.90	76.83	73.10	1.68	2.95	2.17	3.73	77			0.50		79
	3	71.23	75.64	75.31	75.15	70.46	1.08	2.65	1.57	3.42	69	72.6	0.64		49	77
	2	69.06	74.24	74.23	74.07	68.75	1.14	2.17	1.31	2.48	87	70.2	0.61		59	88
	1	66.91	73.10	73.11	72.93	66.53	1.05	2.15	1.22	2.53	86	68.0	0.60		59	85
	V_K			72.08	71.88											

TABLE 1—(CONTINUED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	y_n^*	Y_n[a]	Y_n[c]	x_n^*	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n^* - Y_{n-1}$	$x_{n+1} - x_n^*$	E_o	$x_{a.m.}$	m	R	E	E_{oz}
Medium Concentration Range; Reflux Ratio L/V = ½; Runs C (21-28)																
0.6	L_R	71.0														
	4	64.0	71.5	70.96	71.0	63.2	4.3	7.0	4.8	7.8	90			0.51		90
	3	56.8	67.6	67.14	66.7	54.7	3.5	7.2	4.4	9.3	80	60.4	0.50		59	78
	2	47.8	63.6	63.70	63.2	47.0	4.4	9.0	4.8	9.8	92	52.3	0.42		68	92
	1	36.6	59.3	59.49	58.8	35.3	5.9	11.2	6.4	12.5	92	42.2	0.40		69	90
	V_K			53.94	52.9											
1.0	L_R	70.5														
	4	63.3	71.1	70.57	70.5	62.3	4.1	7.2	4.7	8.2	87			0.50		88
	3	55.8	67.2	66.78	66.4	53.9	3.8	7.5	4.6	9.4	83	59.6	0.48		61	80
	2	46.7	63.1	63.19	62.6	45.8	4.5	9.1	5.0	10.0	90	51.3	0.41		67	91
	1	35.4	58.8	58.87	58.1	33.2	5.7	11.3	6.4	13.5	89	41.1	0.40		67	84
	V_K			53.38	52.4											
1.4	L_R	70.0														
	4	62.6	70.7	70.19	70.0	61.4	4.0	7.4	4.7	8.6	85			0.50		86
	3	54.9	66.8	66.42	66.0	53.1	3.9	7.7	4.7	9.5	83	58.8	0.48		61	81
	2	45.6	62.5	62.69	62.1	44.7	4.6	9.3	5.0	10.2	92	50.3	0.40		69	91
	1	34.3	58.4	58.27	57.5	31.6	5.7	11.3	6.6	14.0	86	40.0	0.41		65	81
	V_K			52.81	51.8											
1.8	L_R	69.6														
	4	62.0	70.3	69.83	69.6	60.7	3.9	7.6	4.6	8.9	85			0.50		
	3	53.9	66.4	66.09	65.7	52.5	4.1	8.1	4.8	9.5	85	58.0	0.47		62	85
	2	44.4	62.0	62.20	61.6	43.5	4.7	9.5	5.1	10.4	92	49.2	0.40		69	91
	1	33.1	58.1	57.66	56.9	30.0	5.6	11.3	6.8	14.4	82	38.8	0.41		63	78
	V_K			52.27	51.3											
2.2	L_R	69.2														
	4	61.4	70.0	69.48	69.2	60.0	3.8	7.8	4.6	9.2	83			0.50		85
	3	53.0	66.0	65.78	65.4	51.9	4.3	8.4	4.9	9.5	88	57.2	0.47		64	88
	2	43.4	61.6	61.72	61.1	42.3	4.8	9.6	5.3	10.7	91	48.2	0.39		69	90
	1	32.0	57.7	57.06	56.3	28.2	5.7	11.4	7.1	15.2	80	37.7	0.41		61	75
	V_K			51.71	50.6											

TABLE 1—(CONCLUDED)
SUMMARY OF EXPERIMENTAL RESULTS

u	n	x_n	y_n^*	Y_n^s	Y_n^c	x_n^*	$Y_n - Y_{n-1}$	$x_{n+1} - x_n$	$y_n^* - Y_{n-1}$	$x_{n+1} - x_n^*$	E_o	$x_{a.m.}$	m	R	E	E_{ox}
Low Concentration Range; Reflux Ratio L/V = ½; Runs B (13-21)																
0.6	L_R	50.9														
	4	19.3	52.1	50.6	50.9	16.9	15.8	31.6	17.0	34.0	93			0.50		93
	3	6.17	36.1	37.0	35.1	5.8	7.5	13.1	8.5	13.5	88	12.8	0.96		51	97
	2	4.01	28.7	29.8	27.6	3.8	1.2	2.2	2.3	2.4	52	5.1	3.4		22	92
	1	3.46	26.2	28.7	26.4	3.5	2.4	0.6	2.2	0.5	109	3.7	4.4		27	120
	V_K			26.4	24.0											
1.0	L_R	47.5														
	4	15.8	50.2	47.7	47.5	12.4	16.2	31.7	18.9	35.1	86			0.50		90
	3	5.17	33.1	33.4	31.3	4.7	6.8	10.6	8.6	11.1	79	10.5	1.4		42	96
	2	3.41	26.0	26.9	24.5	3.1	1.7	1.8	3.2	2.1	53	4.3	3.9		21	86
	1	3.06	24.2	25.3	22.8	2.8	0.1	0.3	1.5	0.6	7	3.2	5.0		5	50
	V_K			25.2	22.7											
1.4	L_R	45.8														
	4	13.8	48.8	46.4	45.8	11.0	16.3	32.0	19.3	34.8	84			0.50		92
	3	4.62	31.2	31.7	29.5	4.2	6.2	9.2	7.9	9.6	79	9.2	1.7		38	96
	2	3.17	24.8	25.8	23.3	2.9	1.1	1.4	2.6	1.7	42	3.8	4.3		18	82
	1	2.91	23.4	24.7	22.2	2.7	0.2	0.3	1.4	0.5	14	3.0	5.3		9	60
	V_K			24.5	22.0											
1.8	L_R	44.7														
	4	12.7	47.8	45.7	44.7	10.2	16.0	32.0	19.1	34.5	84			0.50		93
	3	4.32	30.0	30.9	28.7	4.0	5.9	8.4	7.2	8.7	82	8.5	1.9		37	97
	2	3.03	24.0	25.3	22.8	2.8	1.0	1.3	2.2	1.5	45	3.7	4.4		18	87
	1	2.84	23.0	24.3	21.8	2.6	0.2	0.2	1.4	0.4	14	2.9	5.4		9	50
	V_K			24.1	21.6											
2.2	L_R	44.0														
	4	11.9	46.9	45.4	44.0	9.7	15.6	32.1	18.5	34.3	84			0.50		94
	3	4.19	29.4	30.6	28.4	3.9	5.9	7.7	6.9	8.0	85	8.1	2.1		36	96
	2	3.00	23.7	25.0	22.5	2.8	0.9	1.2	2.1	1.4	43	3.6	4.5		18	86
	1	2.83	23.0	24.2	21.6	2.6	0.3	0.2	1.7	0.4	18	2.9	5.4		10	50
	V_K			23.9	21.3											
2.6	L_R	43.6														
	4	11.5	46.5	45.2	43.6	9.5	15.4	32.1	18.3	34.1	84			0.50		94
	3	4.13	29.2	30.4	28.2	3.9	5.9	7.4	6.9	7.6	85	7.8	2.2		35	97
	2	2.99	23.8	24.8	22.3	2.7	0.7	1.1	2.2	1.4	32	3.6	4.5		15	79
	1	2.85	23.1	24.1	21.6	2.6	0.4	0.1	1.9	0.4	21	2.9	5.4		11	25
	V_K			23.8	21.2											

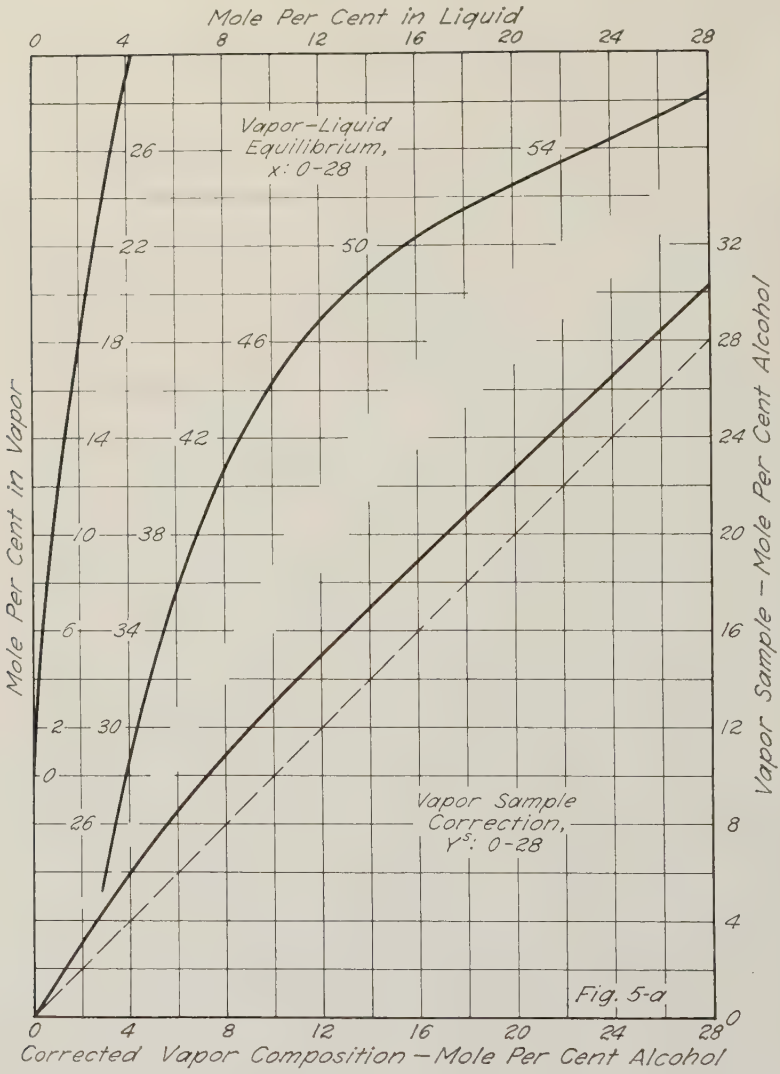


FIG. 5a. VAPOR–LIQUID EQUILIBRIUM RELATIONSHIP AND VAPOR SAMPLE CORRECTION CURVE

Vapor–liquid equilibrium, x:0-28
Vapor sample correction, Y^s:0-28

column, it was judged unnecessary to hold rigorously to this condition in the present work. If, in the rectification of a binary mixture, the two components of the system have significantly different molal heats of vaporization, it is generally possible, as Peters[4] has pro-

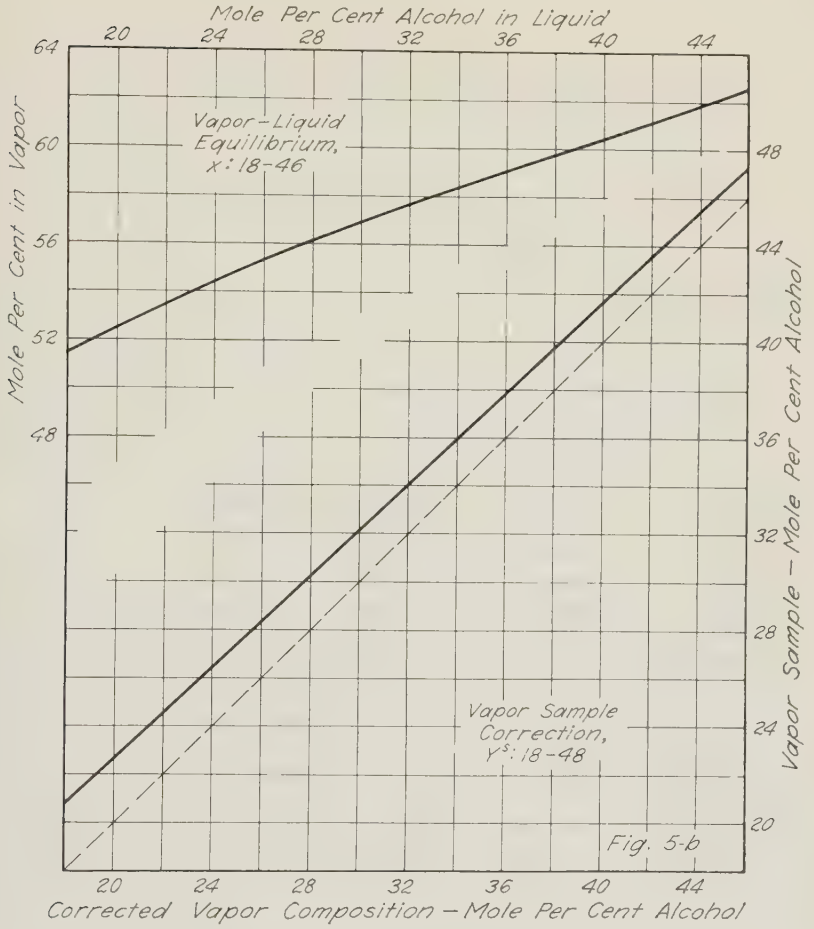


FIG. 5b. VAPOR–LIQUID EQUILIBRIUM RELATIONSHIP AND VAPOR SAMPLE CORRECTION CURVE

Vapor–liquid equilibrium, x:18-46
Vapor sample correction, Y^s:18-46

posed, to adopt one as a basis and assign adjusted values to the other. In this case the boiling-point and equilibrium relationships must be calculated on the basis of the fictitious molecular weight. However, an examination of the values[13] for the molal latent heats of ethyl alcohol (9410 cal. per g. mole at 78 deg. C., 8910 at 100 deg. C.) and of water (9930 cal. per g. mole at 80 deg. C., 9700 at 100 deg. C.) indicates an extreme difference of 11 per cent [(9930 – 8910)/8910] and, in most cases, a difference of approximately 5 per

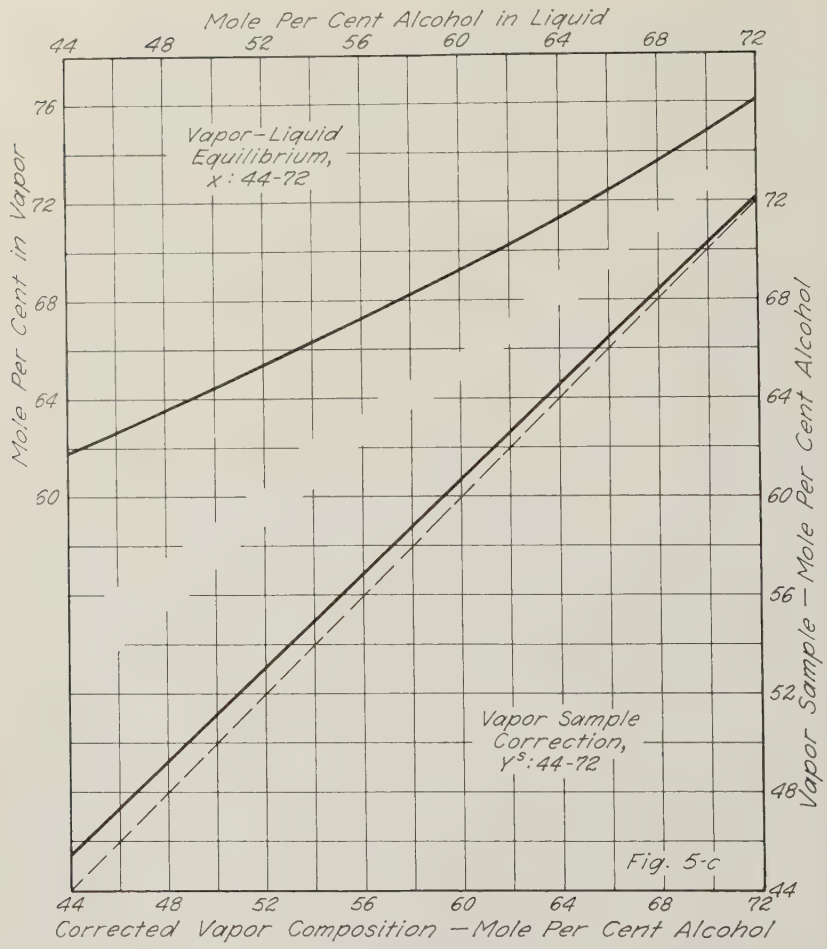


FIG. 5c. VAPOR–LIQUID EQUILIBRIUM RELATIONSHIP AND VAPOR SAMPLE CORRECTION CURVE

Vapor-liquid equilibrium, x:44-72
Vapor sample correction, Y^s:44-72

cent. Under the same experimental conditions of temperature range, the differences in the sensible heats of vapor and liquid and the heat of mixing on the several plates are negligibly small. The results of three runs (A-16, C-29, and B-12) made with no reflux indicate that the heat losses from the insulated apparatus were not appreciable, since there was little enrichment of the vapor stream from plate to plate by partial condensation.

Both the results of the runs at total reflux (in this case the com-

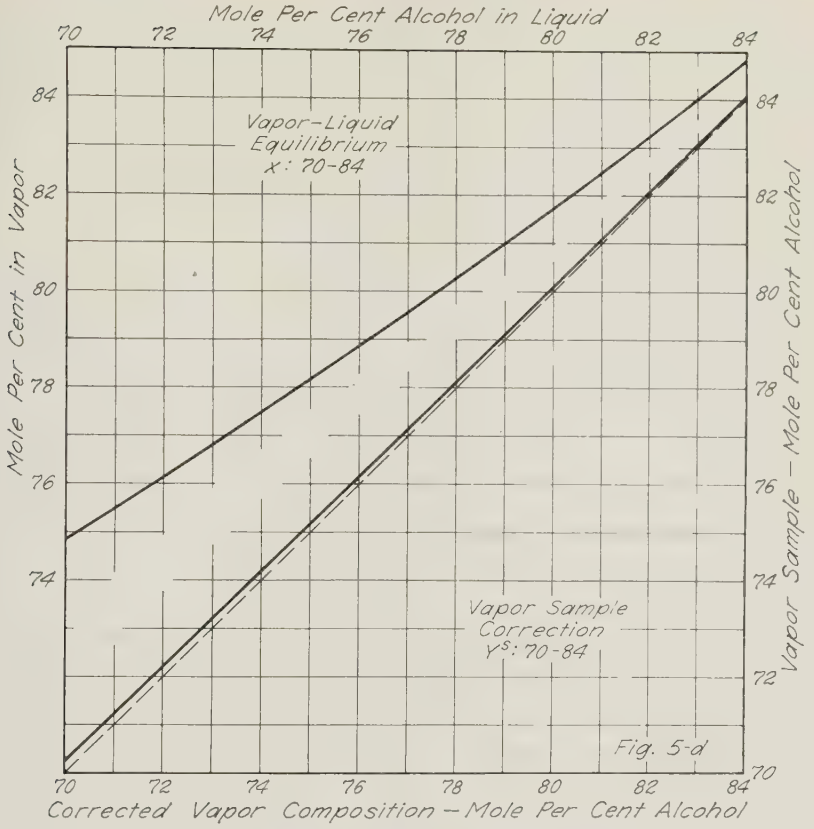
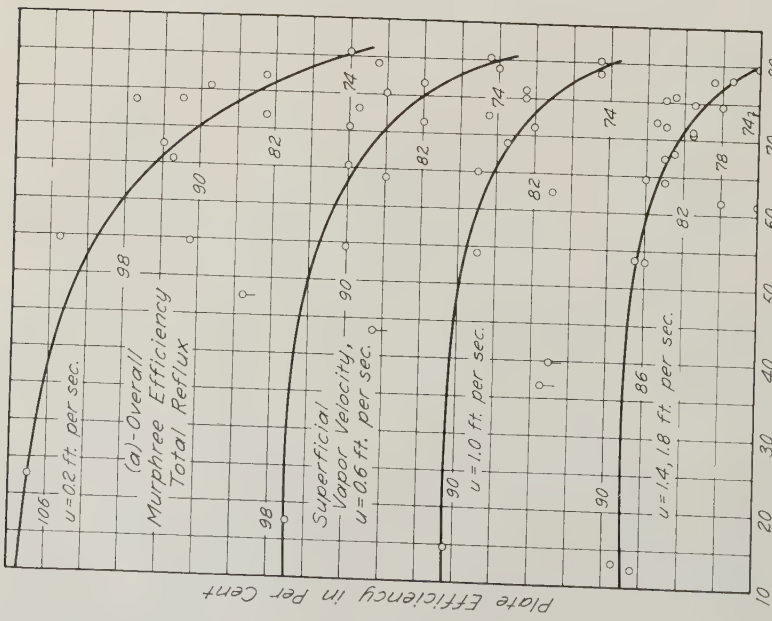


FIG. 5d. VAPOR–LIQUID EQUILIBRIUM RELATIONSHIP AND VAPOR SAMPLE CORRECTION CURVE

Vapor–liquid equilibrium, x:7084
Vapor sample correction, Y^s:70-84

position of the liquid leaving each plate must be, by material balance under ideal conditions, the same as that of the vapor entering), and a comparison of the values for the composition of vapor leaving the top plate and the composition of the condensate indicated that a slight amount of enrichment by partial rectification occurred, in almost every case, in the vapor sampling tubes and lines. It was found that this sample enrichment was independent of the rate of distillation, indicating the absence of entrainment. The enrichment was, however, roughly proportional to the difference, $y^* - x$, between the composition of the condensed sample and its equilibrium vapor. It was then possible to develop the correction curve of Fig. 5, extended to the lower range of composition by extrapolation.



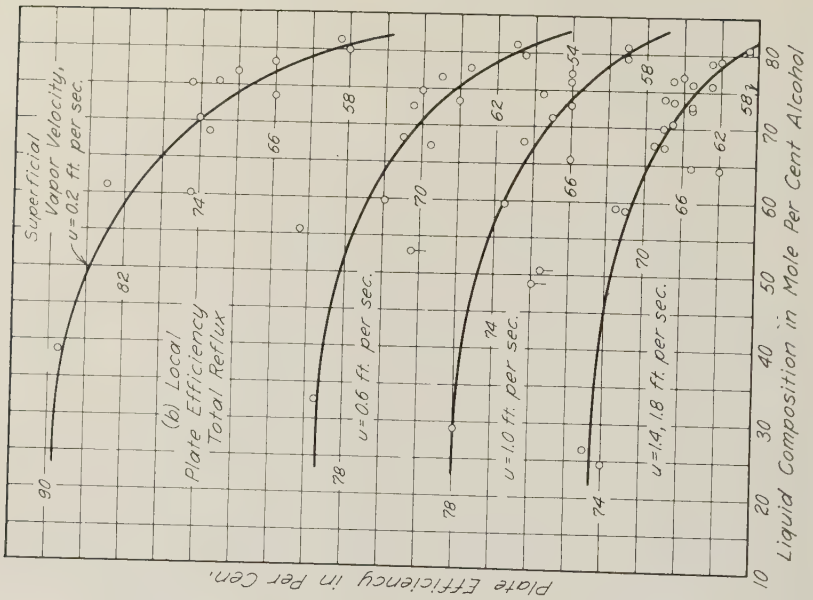


FIG. 6. PLATE EFFICIENCIES, $R = 1$

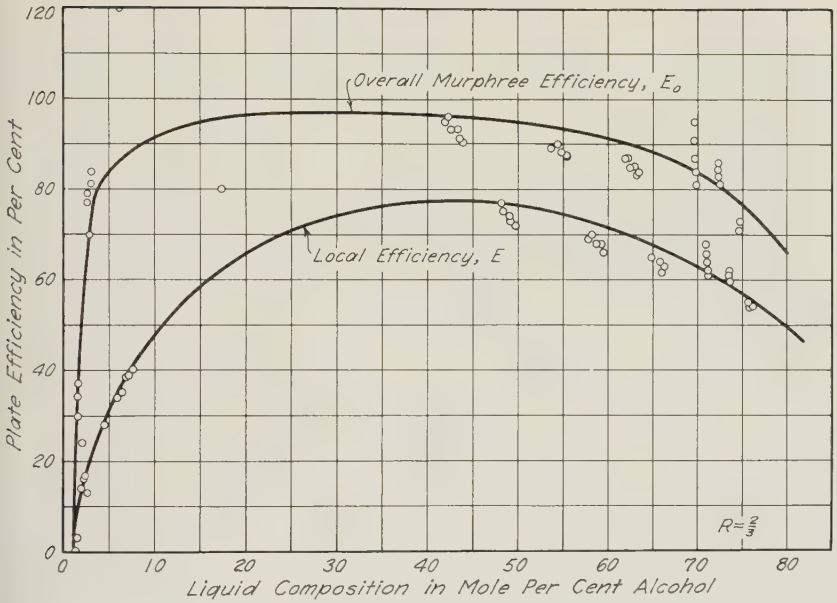


FIG. 7. PLATE EFFICIENCIES, $R = 2/3$

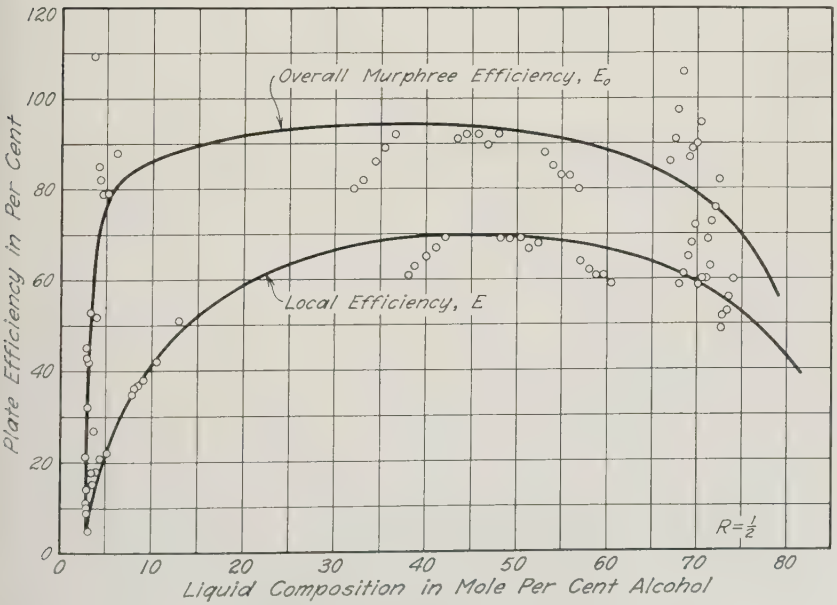


FIG. 8. PLATE EFFICIENCIES, $R = 1/2$

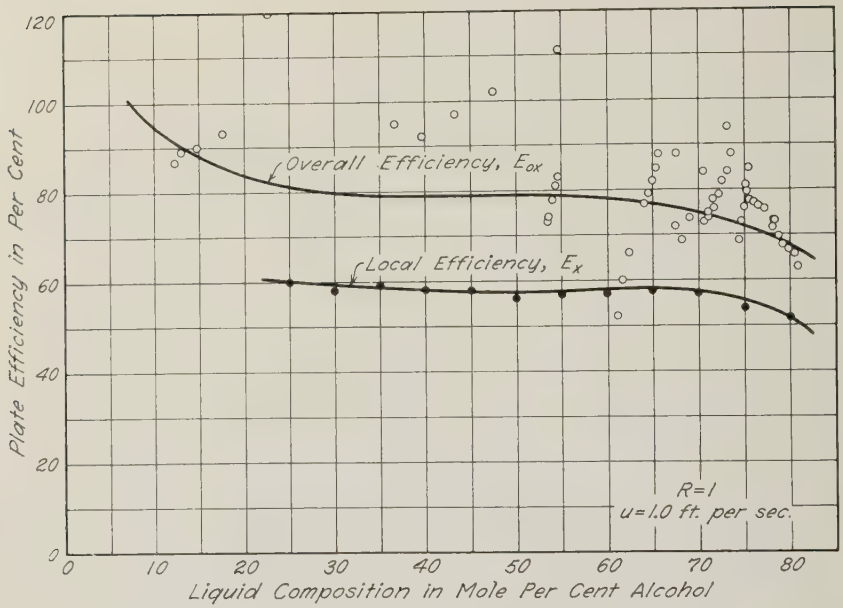


Fig. 9. "Liquid" Plate Efficiencies, $R = 1$

The corrected values of vapor composition $Y_n{}^c$ are tabulated beside the values as sampled, $Y_n{}^s$. The compositions of vapor $y_n{}^*$ in equilibrium with the liquid x_n leaving each plate, and the values of liquid compositions $x_n{}^*$ in equilibrium with the vapor $Y_n{}^c$ leaving each plate, were taken from Table 5 (Appendix) and are also given in Table 1. From these data the overall Murphree plate efficiency in terms of vapor compositions, $E_o = (Y_n - Y_{n-1})/(y_n{}^* - Y_{n-1})$, was directly computed for each case at the several vapor velocities and plotted in Figs. 6a, 7, and 8 as a function of liquid composition.

Since the derivation of the local plate efficiency in terms of vapor compositions, E, as defined by Equation (14), assumed a linear vapor–liquid equilibrium relationship over a short range of liquid composition, it was necessary to approximate this condition by adopting the arithmetic mean of the compositions of liquid entering and leaving each plate, as the basis for choosing the slope of the equilibrium curve m. Each of these average values of liquid composition is given in Table 1, together with the corresponding value of m, as derived from Fig. 5, and with the experimental value of reflux ratio at the top plate, $(L/V)_4$ or R. The values of local efficiency E

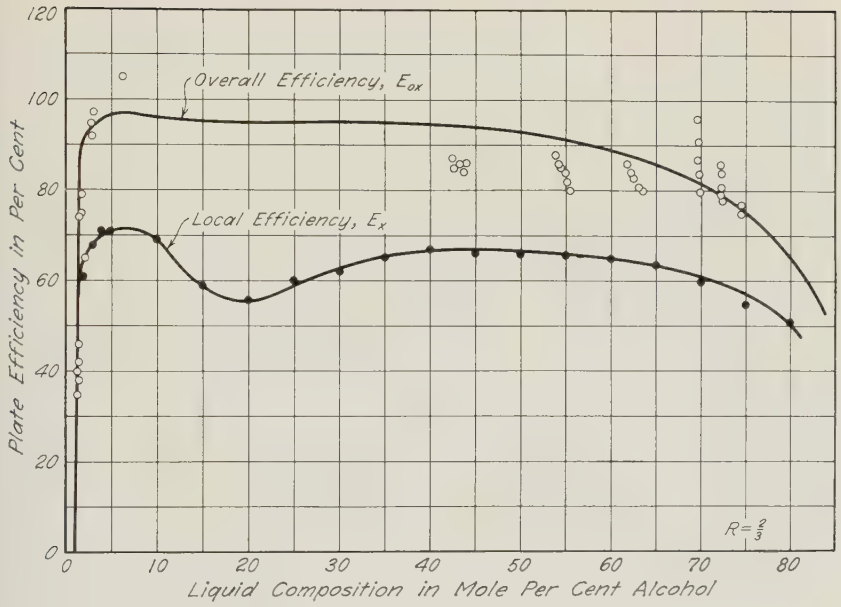


FIG. 10. "LIQUID" PLATE EFFICIENCIES, $R = \frac{2}{3}$

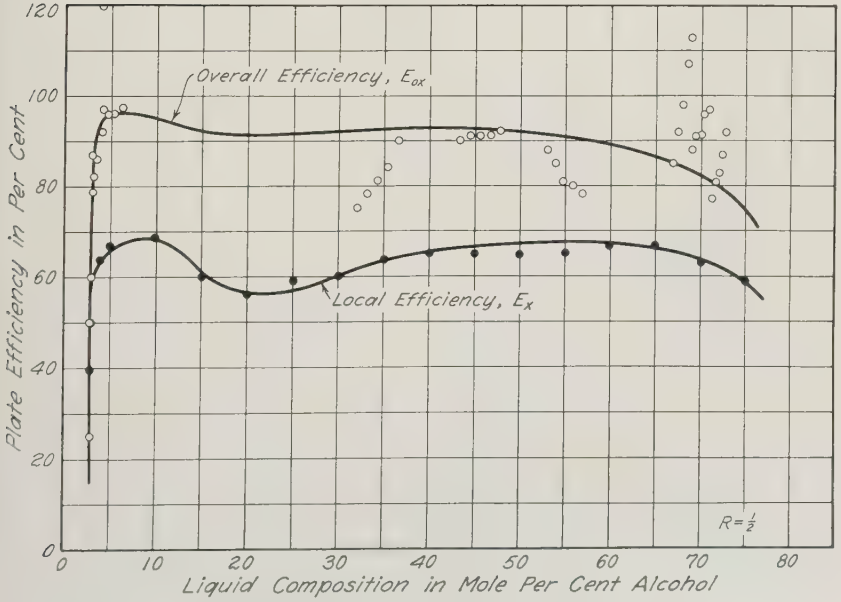


FIG. 11. "LIQUID" PLATE EFFICIENCIES, $R = \frac{1}{2}$

Table 2
Plate Efficiencies in Terms of Liquid Compositions

Nomenclature

E = local plate efficiency in terms of vapor compositions (Figs. 6b, 7, and 8)
E_x = local plate efficiency in terms of liquid compositions, $E/[E + R/m(1 - E)]$, (Figs. 9, 10, and 11)
E_o = overall Murphree efficiency in terms of vapor compositions (Figs. 6a, 7, and 8)
E_{ox} = overall Murphree efficiency in terms of liquid compositions, $E_o/[E_o + R/m(1 - E_o)]$, (Figs. 9, 10, and 11)
m = slope of vapor–liquid equilibrium curve at x, dy^*/dx.
R = reflux ratio at top plate $(L/V)_4$
u = superficial vapor velocity through free space, ft. per sec.
x = liquid composition, mole per cent ethyl alcohol

Subscripts

o = overall (plate efficiency)
x = in terms of liquid compositions (plate efficiency)

x	m	$1/m$	$R = 1$, $u = 1.0$				$R = 0.68$							$R = 0.50$					x
			E_o	E_{ox}	E	E_x	R/m	E_o	$1 - E_o$	E_{ox}	E	$1 - E$	E_x	R/m	E_o	E_{ox}	E	E_x	
0	11.5	0.09					0.06							0.04					
1	8.7	0.12					0.08	0.00	1.00	0.00	0.00	1.00	0.00	0.06					0
2	6.6	0.15					0.10	0.56	0.44	0.92	0.14	0.86	0.61	0.08					1
3	5.3	0.19					0.13	0.73	0.27	0.95	0.21	0.79	0.68	0.09	0.40	0.87	0.06	0.40	2
4	4.1	0.24					0.17	0.81	0.19	0.96	0.29	0.71	0.71	0.12	0.68	0.95	0.18	0.64	3
5	3.6	0.28					0.19	0.84	0.16	0.97	0.31	0.69	0.71	0.14	0.76	0.96	0.22	0.67	4
6	3.0	0.33					0.23	0.86	0.14	0.97				0.17					5
7	2.5	0.40					0.27	0.88	0.12	0.97				0.20					6
8	2.2	0.45					0.31	0.89	0.11	0.97				0.23					7
9	1.8	0.56					0.38	0.90	0.10	0.96				0.28					8
10	1.6	0.63	0.91	0.94			0.43	0.91	0.09	0.96	0.48	0.52	0.69	0.31	0.86	0.95	0.41	0.69	9
11	1.3	0.77					0.52	0.92	0.08	0.96				0.38					10
12	1.1	0.91	0.91	0.92			0.62	0.93	0.07	0.96				0.45					11
13	0.92	1.09					0.74	0.94	0.06	0.96				0.54					12
14	0.84	1.19					0.81	0.94	0.06	0.95				0.60					13
15	0.71	1.41	0.91	0.87			0.96	0.95	0.05	0.95	0.58	0.42	0.59	0.70	0.89	0.92	0.52	0.60	14
16	0.65	1.54					1.05	0.95	0.05	0.95				0.77					15
17	0.60	1.67	0.91	0.86			1.13	0.96	0.04	0.95				0.83					16
18	0.51	1.96					1.33	0.96	0.04	0.95				0.98					17
19	0.45	2.22					1.51	0.96	0.04	0.94				1.11					18
20	0.44	2.27	0.91	0.82			1.54	0.96	0.04	0.94	0.66	0.34	0.56	1.13	0.92	0.91	0.59	0.56	19
																			20

TABLE 2—(CONCLUDED)
PLATE EFFICIENCIES IN TERMS OF LIQUID COMPOSITIONS

x	m	$1/m$	$R = 1$, $u = 1.0$				$R = 0.68$							$R = 0.50$					x
			E_o	E_{ox}	E	E_x	R/m	E_o	$1 - E_o$	E_{ox}	E	$1 - E$	E_x	R/m	E_o	E_{ox}	E	E_x	
25	0.42	2.38	0.91	0.81	0.78	0.60	1.62	0.97	0.03	0.95	0.71	0.29	0.60	1.19	0.93	0.92	0.63	0.59	25
30	0.39	2.57	0.91	0.80	0.78	0.58	1.74	0.97	0.03	0.95	0.74	0.26	0.62	1.28	0.94	0.92	0.66	0.60	30
35	0.41	2.44	0.91	0.80	0.78	0.59	1.66	0.97	0.03	0.95	0.76	0.24	0.65	1.22	0.94	0.93	0.68	0.64	35
40	0.41	2.44	0.91	0.80	0.77	0.58	1.66	0.96	0.04	0.93	0.77	0.23	0.67	1.22	0.94	0.93	0.69	0.65	40
45	0.40	2.50	0.90	0.78	0.77	0.58	1.70	0.96	0.04	0.93	0.77	0.23	0.66	1.25	0.94	0.92	0.70	0.65	45
50	0.41	2.44	0.90	0.79	0.76	0.56	1.66	0.95	0.05	0.92	0.76	0.24	0.66	1.22	0.93	0.91	0.69	0.65	50
55	0.44	2.27	0.89	0.78	0.75	0.57	1.54	0.93	0.07	0.89	0.75	0.25	0.66	1.13	0.91	0.90	0.68	0.65	55
60	0.50	2.00	0.88	0.78	0.73	0.57	1.36	0.91	0.09	0.88	0.72	0.28	0.65	1.00	0.89	0.89	0.67	0.67	60
65	0.57	1.75	0.86	0.77	0.71	0.58	1.19	0.88	0.12	0.86	0.68	0.32	0.64	0.88	0.85	0.87	0.64	0.67	65
70	0.60	1.67	0.84	0.76	0.69	0.57	1.13	0.84	0.16	0.82	0.63	0.37	0.60	0.83	0.79	0.82	0.59	0.63	70
75	0.63	1.59	0.80	0.71	0.65	0.54	1.08	0.77	0.23	0.75	0.57	0.43	0.55	0.79	0.70	0.75	0.53	0.59	75
80	0.71	1.41	0.74	0.67	0.60	0.52	0.96	0.66	0.34	0.67	0.50	0.50	0.51	0.70					80

were calculated from Equation (14) and are plotted in Figs. 6b, 7, and 8 as a function of (arithmetic mean) liquid composition.

The overall plate efficiency in terms of liquid compositions, $E_{ox} = (x_{n+1} - x_n)/(x_{n+1} - x_n^*)$, was computed directly from the data of Table 1 for each case, and its values are tabulated therein. These experimental values of E_{ox} are also plotted for the three reflux ratios, $L/V = 1$, $\frac{2}{3}$, and $\frac{1}{2}$, in Figs. 9, 10, and 11. The curves representing E_{ox} as a function of liquid composition were derived from corresponding values of E_o by means of Equation (8). The data for the curves are given in Table 2. In the case of rectification at total reflux, it was convenient for purposes of comparison to adopt, as a mean, the curve (Fig. 6a) at a superficial vapor velocity of 1.0 ft. per sec.

In a similar manner curves representing local plate efficiency in terms of liquid compositions, E_x, were derived by means of Equation (7) from the curves of Fig. 6b (at a superficial vapor velocity of 1.0 ft. per sec.) and of Figs. 7 and 8, which show E as a function of liquid composition. The values of E_x thus obtained are given in Table 2 and the curves are plotted in Figs. 9, 10, and 11.

III. Discussion of Results

8. *General Discussion.*—In order to make a comparison of overall Murphree efficiencies and local plate efficiencies for varying composition, reflux ratio, and vapor velocity, curves were drawn as shown in Figs. 12 and 13. The data for these curves were taken from Figs. 6, 7, and 8.

It is apparent from these curves that both the overall Murphree efficiency in terms of vapor compositions, E_o, and the local efficiency E vary markedly with composition of the liquid phase in the rectification of mixtures of ethyl alcohol and water. They are not, however, greatly influenced by variations in the reflux ratio or in the superficial vapor velocity (rate of distillation).

It was possible to study almost the entire range of compositions in fractionations at reflux ratios of two-thirds and one-half, but the characteristics of the vapor–liquid equilibrium curve prevented experimental study at total reflux for liquid compositions below 10 to 20 mole per cent alcohol. The upper curves in Figs. 12 and 13 for total reflux ($L/V = 1$) are reproduced from the curves of Fig. 6, which represent graphical averages of data (cf. Table 1), at a superficial velocity of 0.2 ft. per sec. The lower curves in Figs. 12 and 13 are identical with those of Fig. 6 at velocities of 1.4 and 1.8 ft.

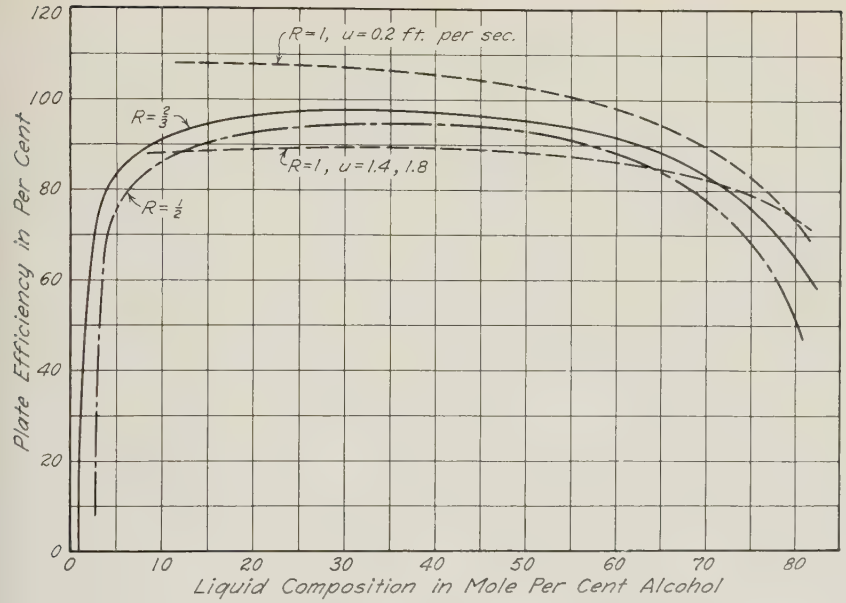


FIG. 12. COMPARISON OF OVERALL MURPHREE EFFICIENCIES

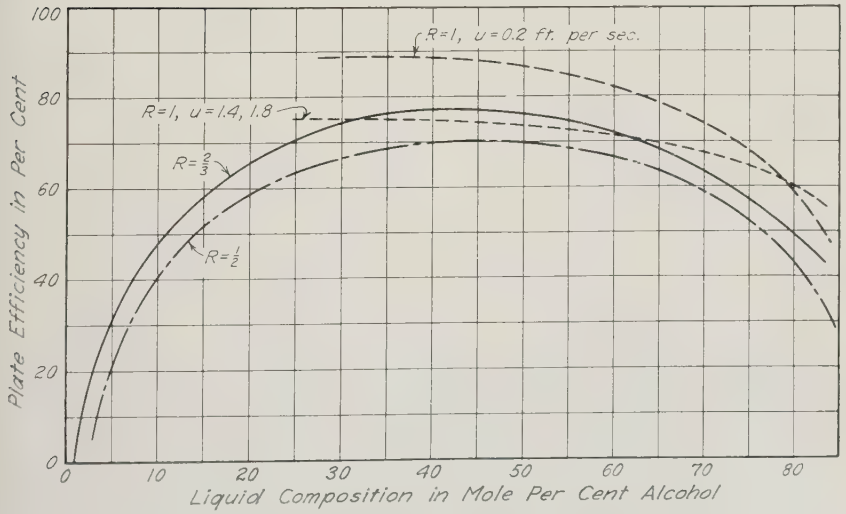


FIG. 13. COMPARISON OF LOCAL PLATE EFFICIENCIES

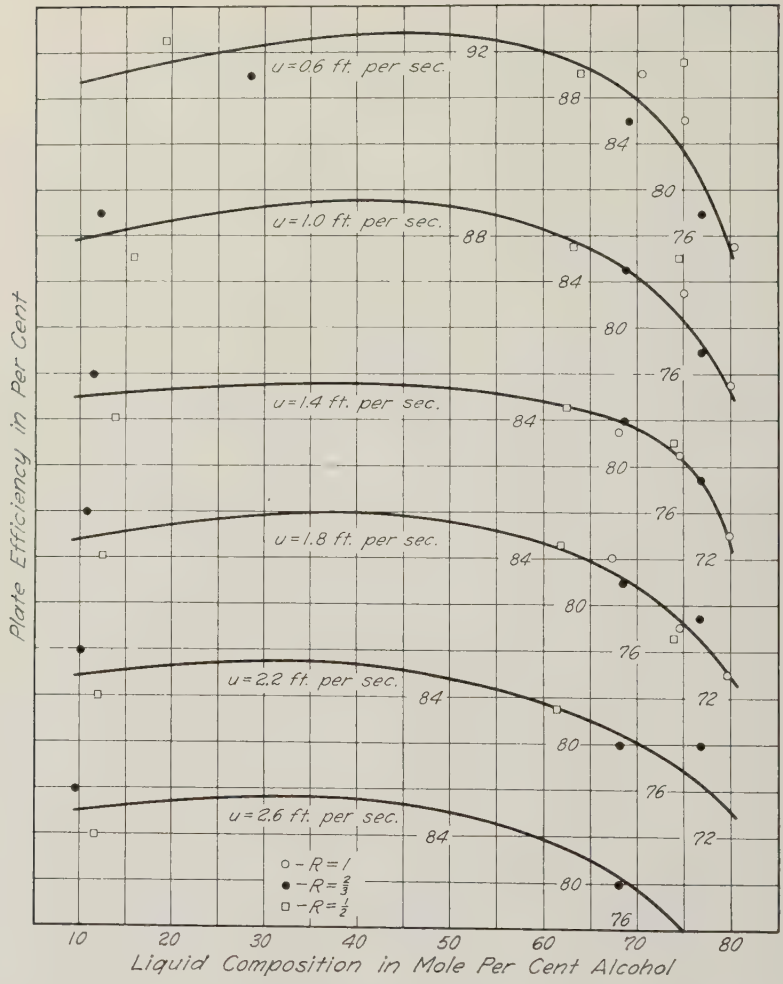

u = 0.6 ft. per sec.
u = 1.0 ft. per sec.
u = 1.4 ft. per sec.
u = 1.8 ft. per sec.
u = 2.2 ft. per sec.
u = 2.6 ft. per sec.
○ - R = 1
● - R = 2/3
□ - R = 1/2
Plate Efficiency in Per Cent
Liquid Composition in Mole Per Cent Alcohol
10 20 30 40 50 60 70 80

Fig. 14. Overall Murphree Efficiency of Top Plate

per sec. Since the data from Table 1 for rectifications at reflux ratios of two-thirds and one-half, when plotted as a function of the liquid composition (cf. Figs. 7 and 8), were closely grouped and manifested no significant or consistent variation with the rate of distillation, it was necessary to plot only two curves for each of these cases as graphical averages of the overall efficiency E_o and of the local efficiency E without regard to vapor velocity. These curves are also reproduced in Figs. 12 and 13 for purposes of comparison.

9. *Overall Murphree and Local Plate Efficiencies.*—It is to be noted that for reflux ratios of two-thirds and one-half, the value of the overall efficiency rises sharply from about 0 to 5 per cent to approximately 80 per cent in the short range of liquid composition, 0 to 10 mole per cent ethyl alcohol. In the same range the local efficiency reaches 50 per cent. The value of the overall efficiency remains near 90 per cent in the range 10 to 60 mole per cent, while the local efficiency reaches the maximum of 70 to 75 per cent at about 50 mole per cent alcohol. The overall efficiency falls to approximately 60 per cent at 80 mole per cent in the liquid, while the local efficiency drops to about 45 per cent. Even at total reflux, as indicated by Figs. 12 and 13, the overall efficiency and local efficiency follow similar trends, but are somewhat greater (5 to 10 per cent) in the range 20 to 80 mole per cent in the liquid.

It must be remembered that neither the overall Murphree efficiency nor the local plate efficiency is a valid representation of plate performance. The truest values of plate efficiency E_m lie in a range between those of the overall and local plate efficiencies. Kirschbaum[21, 29] has proposed a scheme for the computation of the true plate efficiency based on a mean liquid concentration. It is probable that the curves for the local plate efficiency represent more closely the trend of the "median" efficiency E_m than do those for the overall Murphree efficiency.

10. *Influence of Reflux Ratio and Vapor Rate.*—The comparatively minor effect of variations in both reflux ratio and vapor velocity (rate of distillation) on plate efficiency agrees with the qualitative conclusions drawn from observations of bubble-plate operations. When a rectifying column is operated at moderate vapor velocities so that entrainment is absent, it is reasonable to expect that the actual performance of the plate should not be greatly influenced by variations in either the vapor rate or the reflux ratio.

11. *Plate Efficiencies in Terms of Liquid Compositions.*—The concept of an overall plate efficiency in terms of liquid compositions, $E_{ox} = \dfrac{x_{n+1} - x_n}{x_{n+1} - x_n^*}$, which is easily computed from liquid and vapor samples, has no theoretical basis separate from that of E_o based on vapor compositions. Values of E_{ox} may be approximated from corresponding values of E_o by means of Equation (8), as shown in Table 2, and in Figs. 9, 10, and 11.

If values of E_{ox} are known for each plate, or computed from values

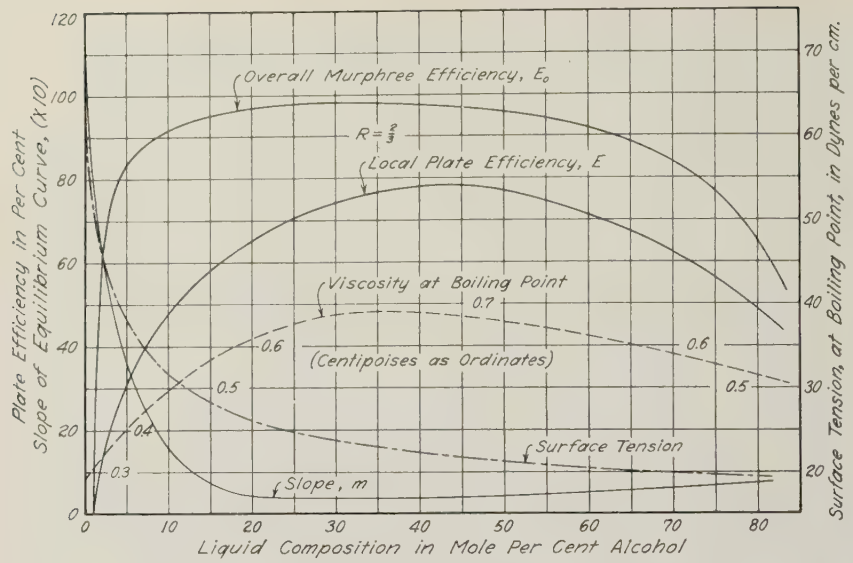


Fig. 15. Plate Efficiencies and Physical Properties of Ethyl Alcohol–Water Mixtures

of E_o, they may be of practical use in calculations of plate column operations in which the change of liquid composition through the column is of greater interest. Moreover, greater precision in experimental determinations of plate efficiency may be possible if computed in terms of liquid compositions directly from vapor and liquid samples, whenever the change in liquid concentration on the plate is appreciably greater than the vapor enrichment through the plate, and when the ideal change in liquid concentration is correspondingly greater than the maximum vapor enrichment theoretically possible. The former condition will be true at reflux ratios less than one, while the latter will generally be significant at high concentrations and low reflux ratios.

Ragatz, Nyland, Souders, and Brown[19] have pointed out that the computation of individual plate efficiencies is an inherently unsatisfactory procedure. The calculation involves the subtraction of two numbers which are, in general, of the same order of magnitude, and the subsequent division of the remainder by another value similarly derived. The calculated values of the efficiencies are therefore extremely sensitive to errors in sampling and analysis as well as in the data for the vapor–liquid equilibrium relationship.

The lower curves of Figs. 9, 10, and 11 represent E_x as a func-

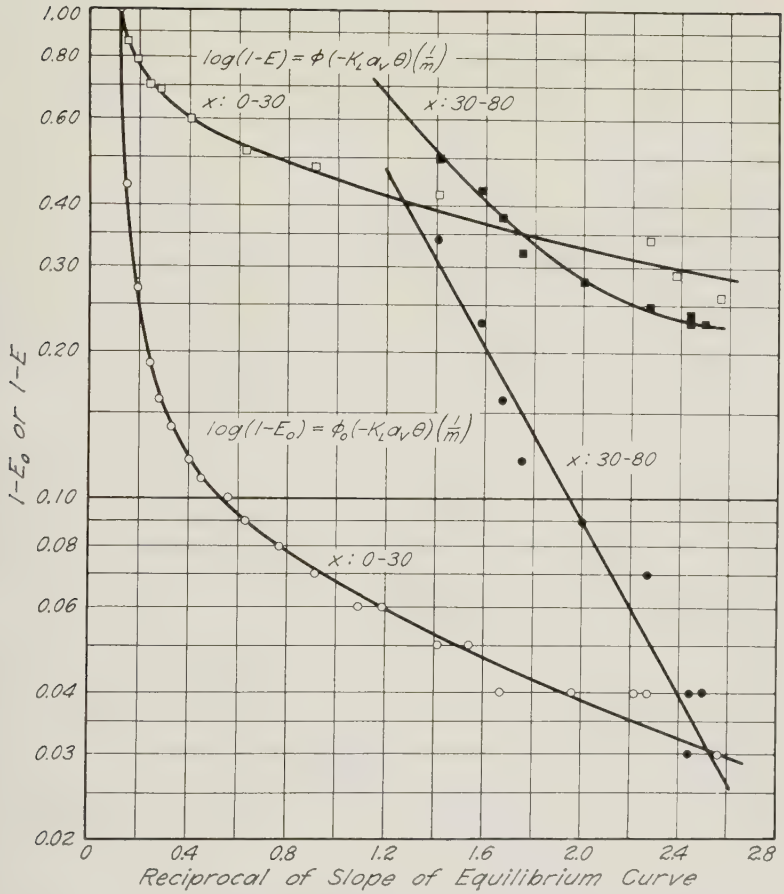


FIG. 16. PLATE EFFICIENCY AS FUNCTION OF SLOPE OF VAPOR–LIQUID EQUILIBRIUM CURVE

tion of liquid composition, as derived from E according to Equation (7), and are plotted from the computed data of Table 2, to be compared with the curves of the overall "liquid" efficiency E_{ox}. The dip which occurs in each of the curves of Figs. 10 and 11 at about 20 mole per cent is a result, primarily, of the rapidly decreasing value of m, the slope of the equilibrium curve (cf. Equation (7)). As E continues to increase and m remains fairly constant, E_x again rises in value to about 70 per cent, falling off with E beyond 60 mole per cent.

12. *Influence of the Physical Properties of the Liquid.*—The influence of viscosity on the size of gas bubbles in contact with a body

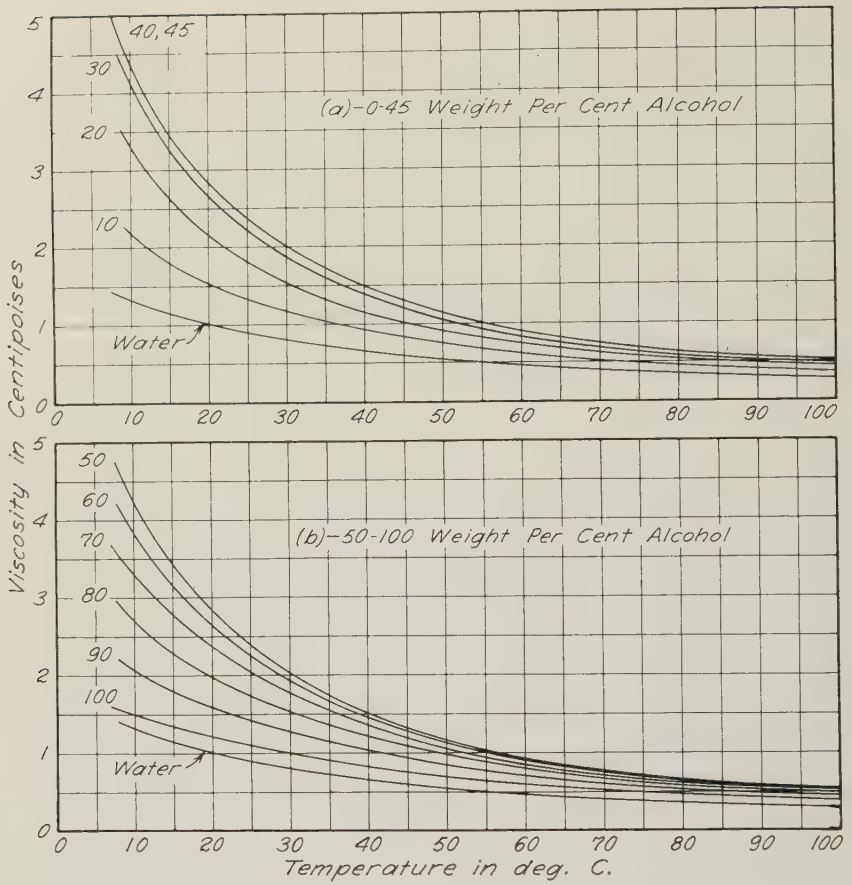


FIG. 17. VISCOSITY OF ETHYL ALCOHOL–WATER MIXTURES

of liquid has been reported by Schnurmann[14, 32] for various mixtures, including those of ethyl alcohol and water. In these investigations a gas saturated with a liquid was forced through porous plates or capillary inlets into a liquid mixture, forming a mass of bubbles. In general, the size of the bubbles was independent of the manner in which they were introduced, even when formed by agitation of the liquid in a closed vessel, but depended consistently on the viscosity. The bubble size varied inversely with the viscosity, and a maximum in the viscosity–composition curve corresponded to a minimum in bubble size. The results of this study indicated that the surface tension of the liquid had no effect on bubble size.

In Fig. 15 are shown both the viscosity and surface tension of

Table 3
Viscosity and Surface Tension of Ethyl Alcohol–Water Mixtures

Nomenclature

t = temperature, deg. C.
W = composition of liquid, weight per cent alcohol
x = composition of liquid, mole per cent alcohol
γ = surface tension of liquid[41], dynes per cm.
μ = viscosity of liquid[13], centipoises, (cf. Fig. 17)

Subscripts

b = at boiling point of liquid[8] (760 mm. Hg.)
t = at indicated temperature

W	x	Temperature t, deg. C.										μ_b	γ_b
		10	20	25	30	40	50	60	70	80	90		
Water	0.00	1.308	1.005	0.894	0.801	0.656	0.549	0.469	0.406	0.357	0.317	0.284	60.4
										t_b		(Fig. 17)	
10	4.16	2.162	1.548	1.328	1.153	0.896	0.725	0.602	0.509	91.5		0.40	41.1
20	8.91	3.235	2.168	1.808	1.539	1.144	0.896	0.728	0.606	86.0		0.49	32.5
30	14.35	4.095	2.670	2.203	1.849	1.353	1.038	0.826	0.677	83.8		0.55	28.3
40	20.68	4.355	2.867	2.374	1.991	1.455	1.116	0.887	0.724	82.3		0.62	26.0
45	24.24	4.310	2.867	2.387	2.007	1.478	1.138	0.902	0.736	81.8		0.62	25.1
50	28.11	4.174	2.832	2.368	2.001	1.475	1.136	0.904	0.739	81.3		0.68	24.5
60	36.97	3.787	2.642	2.232	1.906	1.426	1.109	0.887	0.727	80.5		0.69	23.3
70	47.71	3.268	2.369	2.025	1.744	1.328	1.044	0.841	0.696	79.7		0.60	22.0
80	61.00	2.663	1.998	1.738	1.519	1.181	0.950	0.778	0.648	79.0		0.58	20.8
90	77.87	2.048	1.601	1.422	1.270	1.022	0.835	0.695	0.589	78.2		0.53	19.6
100	100.00	1.480	1.221	1.101	0.997	0.824	0.695	0.590	0.506	78.1		0.47	18.4

ethyl alcohol–water mixtures (at the boiling point) as functions of liquid composition. These curves were developed from the data of Table 3 and from Fig. 17.

The formation of heavy froth or foam below the point of appreciable entrainment has been considered by designers as a necessary condition in order to maintain high plate efficiencies. The increase in total area of vapor–liquid contact with greater depths of foam may be considered a primary result of the increased proportion of surface area to volume of vapor, with decreasing bubble size. If, as has been suggested, the greater part of the material transfer in plate rectification occurs in the formation and breaking of vapor bubbles in the agitated liquid, the viscosity of the liquid should be an important controlling factor insofar as it affects the size of vapor bubbles.

A comparison of the trend of the viscosity–composition relationship of Fig. 15 with that of the two efficiency curves gives partial confirmation to these tentative conclusions. If the curves of E_o and E are considered as limiting the range of the "median" efficiency E_m, the value of the latter may be expected to reach a maximum at about the same value of liquid composition as does the viscosity—in this case between 20 and 40 mole per cent alcohol.

Figures 6, 7, 8, 12, and 13 indicate that low plate efficiencies exist at the extremes of the composition range where the maximum available diffusional driving force, $y_n^* - Y_{n-1}$, is small (cf. Figs. 1 and 5). This rapid decrease in Murphree efficiency at very low and at high concentrations of ethyl alcohol cannot be definitely attributed to the influence of liquid composition (or its physical properties) because of the lack of precision inherent in plate efficiency computations, as has previously been noted[19].

IV. Summary

A study has been made of the fractional distillation of ethyl alcohol–water mixtures in a bubble-cap column of four plates, operated without entrainment at superficial vapor velocities, $u = 0.2$ to $u = 3$ ft. per sec., and at reflux ratios, $L/V = 1$, $\frac{2}{3}$, and $\frac{1}{2}$.

The determination of plate efficiencies, by direct computation from compositions of both vapor and liquid samples, has been shown to be both experimentally practicable and valuable in theoretical studies.

Both the overall Murphree E_o and the local plate efficiency E, in terms of vapor compositions, vary markedly with liquid composition over its entire range, but are not significantly affected by varia-

tions in reflux ratio or in the rate of distillation. In general, the value of the overall Murphree efficiency rises sharply from 0 to 5 per cent to approximately 85 per cent in the range of liquid composition, 0 to 10 mole per cent alcohol; it varies between 80 and 100 per cent from 10 to 60 mole per cent alcohol, and then decreases to about 60 per cent at 80 mole per cent alcohol. The local plate efficiency increases to 70 to 80 per cent at 40 to 50 mole per cent alcohol, and then decreases to about 50 per cent at 80 mole per cent alcohol in the liquid.

The corresponding efficiencies in terms of liquid compositions, E_{ox} and E_x, which are frequently of practical interest, have also been calculated and are compared with the "vapor" efficiencies.

A comparison has been made between the efficiency curves and the curve representing the change of viscosity with liquid composition. The similarity of trend of the two curves indicates that the maximum plate efficiency may occur in this particular system (ethyl alcohol–water) at the point of maximum viscosity.

The apparent conclusion, that the low plate efficiencies found at the extremes of the concentration range (where the available diffusional driving force is small) is due to the influence of liquid composition, is not justified because of the lack of precision inherent in the calculation of the Murphree efficiency.

Appendix

1. Physical Data for Ethyl Alcohol–Water Mixtures.—

Table 4

Physical Data (Ethyl Alcohol–Water)

Nomenclature

d = density in vacuo of ethyl alcohol–water mixtures[23] at 35 deg. C., g. per ml.
d' = density difference (for interpolation), g. per ml.
t_b = boiling point[3] at 760 mm. Hg, deg. C.
W = composition of liquid, weight per cent alcohol
x = composition of liquid, mole per cent alcohol
y_W^* = composition of vapor in equilibrium with liquid[9], weight per cent alcohol

W	d	d'	x	y_W^*	t_b
0	0.99406	0.00189	0.00	0.0	100.00
1	217	186	0.39	10.5	98.88
2	031	182	0.79	18.5	97.88
3	0.98849	177	1.20	26.3	96.92
4	672	171	1.60	31.2	96.05
5	501	166	2.02	36.0	95.18
6	335	163	2.44	39.8	94.34
7	172	163	2.86	43.3	93.55
8	009	163	3.29	46.3	92.83
9	0.97846	161	3.72	49.2	92.13
10	685	158	4.16	51.6	91.45
11	527	156	4.61	53.6	90.82
12	371	155	5.06	55.5	90.18
13	216	153	5.52	57.0	89.57
14	063	152	5.99	58.6	88.97
15	0.96911	151	6.46	60.0	88.40
16	760	153	6.93	61.2	87.85
17	607	155	7.42	62.4	87.34
18	452	158	7.91	63.5	86.86
19	294	160	8.40	64.5	86.42
20	134	161	8.91	65.5	86.03
21	0.95973	164	9.42	66.3	85.70
22	809	166	9.93	67.0	85.40
23	643	167	10.46	67.7	84.90
24	476	170	10.99	68.4	84.90
25	306	173	11.53	69.0	84.68
26	133	178	12.08	69.5	84.47
27	0.94955	0.00181	12.64	70.0	84.27
28	774	184	13.20	70.5	84.09
29	590	187	13.77	70.9	83.91
30	403	189	14.35	71.2	83.75
31	214	193	14.94	71.6	83.60
32	021	196	15.54	71.9	83.48
33	0.93825	199	16.15	72.2	83.28
34	626	201	16.77	72.5	83.12
35	425	204	17.39	72.8	82.98
36	221	205	18.03	73.1	82.84
37	016	208	18.68	73.4	82.70
38	0.92808	211	19.33	73.6	82.56
39	597	212	20.00	73.8	82.43
40	385	215	20.68	74.0	82.30
41	170	218	21.37	74.3	82.19
42	0.91952	219	22.07	74.6	82.08
43	733	220	22.78	74.9	81.97
44	513	222	23.50	75.2	81.86
45	291	222	24.24	75.4	81.76
46	069	224	24.99	75.7	81.67
47	0.90845	224	25.75	75.9	81.58
48	621	225	26.52	76.2	81.49
49	396	228	27.31	76.4	81.40
50	168	228	28.11	76.7	81.31

TABLE 4—(CONCLUDED)
PHYSICAL DATA (ETHYL ALCOHOL–WATER)

W	d	d'	x	y_W*	t_b
51	0.89940	230	28.93	76.9	81.23
52	710	231	29.76	77.1	81.15
53	479	231	30.60	77.3	81.07
54	248	232	31.46	77.5	80.99
55	016	232	32.34	77.8	80.91
56	0.88784	232	33.23	78.0	80.83
57	552	233	34.14	78.2	80.75
58	319	234	35.07	78.4	80.67
59	085	234	36.01	78.7	80.58
60	0.87851	236	36.97	78.9	80.50
61	610	236	37.95	79.1	80.42
62	379	237	38.95	79.3	80.34
63	142	237	39.97	79.6	80.26
64	0.86905	238	41.01	79.9	80.18
65	667	238	42.07	80.0	80.10
66	429	239	43.15	80.3	80.02
67	190	240	44.26	80.6	79.94
68	0.85950	0.00240	45.39	80.9	79.87
69	710	240	46.54	81.3	79.80
70	470	242	47.71	81.7	79.72
71	228	242	48.91	82.0	79.64
72	0.84986	243	50.14	82.4	79.56
73	743	243	51.39	82.7	79.48
74	500	243	52.68	83.1	79.41
75	257	244	53.99	83.5	79.34
76	013	245	55.33	83.8	79.26
77	0.83768	245	56.70	84.2	79.18
78	523	246	58.10	84.6	79.10
79	277	248	59.53	85.0	79.02
80	029	249	61.00	85.5	78.95
81	0.82780	250	62.51	86.0	78.87
82	530	251	64.05	86.5	78.80
83	279	252	65.63	87.1	78.72
84	027	253	67.25	87.5	78.65
85	0.81774	255	68.91	88.0	78.57
86	519	257	70.61	88.6	78.50
87	262	259	72.35	89.2	78.43
88	003	261	74.15	89.8	78.37
89	0.80742	264	75.98	90.5	78.30
90	478	267	77.87	91.2	78.24
91	211	270	79.81	91.9	78.19
92	0.79941	272	81.81	92.6	78.14
93	669	276	83.90	93.4	78.10
94	393	279	85.97	94.2	78.06
95	114	283	88.14	95.0	78.04
96	0.78831	289	90.37	....	78.04
97	542	295	92.67	....	78.06
98	247	301	95.04	....	78.08
99	0.77946	305	97.48	....	78.10
100	641	...	100.00	....	78.13

Table 5
Physical Data (Ethyl Alcohol–Water)

Nomenclature

d = density in vacuo of ethyl alcohol–water mixtures at 35 deg. C., g. per ml.
d' = density difference (for interpolation), g. per ml.
t_b = boiling point at 760 mm. Hg, deg. C.
x = composition of liquid, mole per cent alcohol
y^* = composition of vapor in equilibrium with liquid, mole per cent alcohol
$(y^*)'$ = equilibrium vapor composition difference (for interpolation), mole per cent

x	d	d'	y^*	$(y^*)'$	t_b
0	0.99406	0.00469	0.00	10.19	100.0
1	0.98937	428	10.19	7.69	97.3
2	509	396	17.88	5.83	95.2
3	113	370	23.71	5.00	93.3
4	0.97743	349	28.71	3.85	91.7
5	394	334	32.56	3.10	90.3
6	060	325	35.66	2.66	89.0
7	0.96735	324	38.32	2.36	87.9
8	411	324	40.68	2.08	86.8
9	087	322	42.76	1.60	86.0
10	0.95765	321	44.36	1.50	85.4
11	444	321	45.86	1.18	84.9
12	123	319	47.04	1.05	84.5
13	0.94804	318	48.09	0.85	84.1
14	486	318	48.94	0.75	83.9
15	168	316	49.69	0.61	83.6
16	0.93852	315	50.30	0.60	83.3
17	537	315	50.90	0.61	83.0
18	222	313	51.51	0.53	82.8
19	0.92909	312	52.04	0.38	82.6
20	597	312	52.42	0.44	82.4
21	285	311	52.86	0.57	82.2
22	0.91974	308	53.43	0.55	82.1
23	666	303	53.98	0.47	81.9
24	363	297	54.45	0.48	81.8
	066	294	54.93	0.40	81.7
26	0.90772	0.00288	55.33	0.44	81.6
27	484	285	55.77	0.46	81.4
28	199	278	56.23	0.36	81.3
29	0.89921	277	56.59	0.33	81.2
30	644	272	56.92	0.33	81.1
31	372	266	57.25	0.40	81.0
32	106	262	57.65	0.38	80.9
33	0.88844	256	58.03	0.31	80.8
34	588	252	58.34	0.32	80.8
35	336	248	58.66	0.44	80.7
36	088	244	59.10	0.30	80.6
37	0.87844	241	59.40	0.29	80.5
38	603	236	59.69	0.30	80.4
39	367	232	59.99	0.44	80.3
40	135	228	60.43	0.42	80.3
41	0.86907	224	60.85	0.13	80.2
42	683	221	60.98	0.41	80.1
43	462	216	61.39	0.41	80.0
44	246	213	61.80	0.41	80.0
45	033	210	62.21	0.47	79.9

TABLE 5—(CONCLUDED)
PHYSICAL DATA (ETHYL ALCOHOL–WATER)

x	d	d'	y^*	$(y^*)'$	t_b
46	0.85823	207	62.68	0.54	79.8
47	616	204	63.22	0.48	79.8
48	412	201	63.70	0.40	79.7
49	211	197	64.10	0.50	79.6
50	014	195	64.60	0.41	79.6
51	0.84819	191	65.01	0.45	79.5
52	628	186	65.46	0.49	79.4
53	442	184	65.95	0.49	79.4
54	258	183	66.44	0.37	79.3
55	075	182	66.81	0.44	79.3
56	0.83893	177	67.25	0.48	79.2
57	716	175	67.73	0.47	79.2
58	541	173	68.20	0.51	79.1
59	368	170	68.71	0.47	79.0
60	198	169	69.18	0.58	79.0
61	029	165	69.76	0.56	79.0
62	0.82864	164	70.32	0.57	78.9
63	700	162	70.89	0.56	78.9
64	538	159	71.45	0.66	78.8
65	379	158	72.11	0.58	78.8
66	0.82221	0.00144	72.69	0.45	78.8
67	066	153	73.14	0.53	78.7
68	0.81913	153	73.67	0.53	78.6
69	760	150	74.20	0.66	78.6
70	610	149	74.86	0.63	78.6
71	461	147	75.49	0.64	78.5
72	314	146	76.13	0.64	78.5
73	168	143	76.77	0.63	78.4
74	025	143	77.40	0.72	78.4
75	0.80882	143	78.12	0.74	78.3
76	739	140	78.86	0.72	78.3
77	599	139	79.58	0.73	78.3
78	460	138	80.31	0.72	78.2
79	322	137	81.03	0.72	78.2
80	185	136	81.75	0.73	78.2
81	049	134	82.48	0.73	78.1
82	0.79915	133	83.21	0.81	78.1
83	782	132	84.02	0.79	78.1
84	650	131	84.81	0.79	78.1
85	519	130	85.60	0.83	78.1
86	389	129	86.43	0.80	78.0
87	260	128	87.23	0.80	78.0
88	132	127	88.03	....	78.0
89	005	127	.....	....	78.0
90	0.78878	126	.....	....	78.0
91	752	126	.....	....	78.0
92	626	125	.....	....	78.0
93	501	125	.....	....	78.1
94	376	124	.....	....	78.1
95	252	124	.....	....	78.1
96	128	123	.....	....	78.1
97	005	122	.....	....	78.1
98	0.77883	121	.....	....	78.1
99	762	121	.....	....	78.1
100	641	...	.....	....	78.1

2. *Bibliography.—*

No.	Year	Author	Reference
1	1899	Sorel	"Distillation et Rectification Industrielles", Paris, Carrié et Naud.
2	1921	Ponchon	Technique moderne, **13**, 20, 55.
3	1922	Fouché	Mém. Soc. Ing. Civils de France, p. 64.
4	1922	Peters, W. A., Jr.	Ind. Eng. Chem., **14**, 476-479.
5	1922	Savarit	Arts métiers, pp. 65, 142, 178, 241, 266, 307.
6	1925	McCabe, W. L., and Thiele, E. W.	Ind. Eng. Chem., **17**, 605-611.
7	1925	Murphree, E. V.	Ind. Eng. Chem., **17**, 747-750.
8	1925	Öman, E., and Gunnelius, A.	Tek. Tid., Uppl. C, **55**, 33.
9	1926	Hausbrand, E.	"Principles and Practice of Industrial Distillation," trans. 4th ed., E. H. Tripp, New York, John Wiley and Sons.
10	1927	Shirk, L. H., and Montonna, R. E.	Ind. Eng. Chem., **19**, 907-911.
11	1928	Thormann	"Destillieren und Rektifizieren."
12	1928	Lewis, W. K., and Chang, K. C.	Trans. Am. Inst. Chem. Engrs., **21**, 127-138.
13	1929		"International Critical Tables," Vol. 5, 1st ed., New York, McGraw-Hill Book Co.
14	1929	Schnurmann, R.	Z. physik. Chem., **143**, 456-474.
15	1930	Baker, T., and Stockhardt, J. S.	Ind. Eng. Chem., **22**, 376-377.
16	1932	Underwood, A. J. V.	Trans. Inst. Chem. Engrs., (London), **10**, 112-152.
17	1933	Carey, J. S., Griswold, J., Lewis, W. K., and McAdams, W. H.	Trans. Am. Inst. Chem. Engrs., **30**, 504-519.
18	1933	Kirschbaum, E.	Chem. Fabrik, **6**, 431-436.
19	1933	Ragatz, E. G., Nyland, H. V., Souders, M., Jr., and Brown, G. G.	Trans. Am. Inst. Chem. Engrs., **30**, 477-503.
20	1934	Chilton, T. H., and Colburn, A. P.	(a) Ind. Eng. Chem., **26**, 1183-1187, (b) Ind. Eng. Chem., **27**, 255-260.
21	1934	Kirschbaum, E.	Forsch. Gebiete Ingenieurw., **5**, 245-252.
22	1934	Kirschbaum, E.	Ann. Physik, **20**, 261-278.

No.	Year	Author	Reference
23	1934	Perry, J. H.	"Chemical Engineers' Handbook," 1st ed., New York, McGraw-Hill Book Co., (Section on Distillation).
24	1936	Gadwa, T. A.	Sc.D. Thesis, Massachusetts Institute of Technology.
25	1936	Hodgman, C. D.	"Handbook of Chemistry and Physics," 21st ed., Cleveland, Ohio, Chemical Rubber Publishing Co., (a) p. 827, (b) p. 1206, (c) p. 1320.
26	1936	Kirschbaum, E., and Andrews, C. A.	J. Inst. Petrol. Tech., **22**, 803-820.
27	1936	Lewis, W. K., Jr.	Ind. Eng. Chem., **28**, 399-401.
28	1936	Uchida, S., and Matsumoto, K.	J. Soc. Chem. Ind. Japan, **39**, suppl. bind., 224B-227B.
29	1937	Kirschbaum, E., and Quade, W.	Forsch. Gebiete Ingenieurw., **8**, 63-67.
30	1937	Peavy, C. C., and Baker, E. M.	Ind. Eng. Chem., **29**, 1056-1064.
31	1937	Rhodes, F. H., and Slachman, P. G.	Ind. Eng. Chem., **29**, 51-55.
32	1937	Schnurmann, R.	Kolloid-Z., **80**, 148-151.
33	1937	Sherwood, T. K.	"Absorption and Extraction," 1st ed., New York, McGraw-Hill Book Co., (a) p. 10, (b) p. 23, (c) p. 43, (d) p. 62, (e) p. 86.
34	1938	Keyes, D. B.	Circular 35, Engineering Experiment Station, University of Illinois.
35	1938	Kirschbaum, E.	Z. Ver. deut. Ing., suppl. Verfahrenstechnik, No. 5, 131-139.
36	1939	Langdon, W. M.	M.S. Thesis, University of Illinois.
37	1939	Robinson, C. S., and Gilliland, E. R.	"The Elements of Fractional Distillation," 3rd ed., New York, McGraw-Hill Book Co., (a) p. 208, (b) p. 209.
38	1939	Schoenborn, E. M., Jr., and Colburn, A. P.	Trans. Am. Inst. Chem. Engrs., **35**, 359-389.
39	1939	Sherwood, T. K., and Reed, C. E.	"Applied Mathematics in Chemical Engineering," 1st ed., pp. 40-43, New York, McGraw-Hill Book Co.
40	1940	Kirschbaum, E.	"Destillier und Rektifiziertechnik."
41	1940	Bonnell, W. S., Byman, L., and Keyes, D. B.	Ind. Eng. Chem., **32**, 532-534.
42	1940	Furnas, C. C., and Taylor, M. L.	Trans. Am. Inst. Chem. Engrs., **36**, 135-171.

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